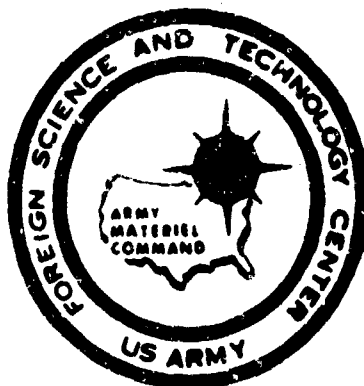


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PART I - PHYSICO-CHEMICAL PHENOMENA ASSOCIATED WITH THE

ACTION OF LIQUID METALS ON SOLIDS

PART II - MECHANISM OF REACTION OF LIQUID METALS

ON SOLIDS IN A STRESSED STATE

by

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SUBJECT COUNTRY: USSR



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13. ABSTRACT In Part I, the book discusses the processes associated with the action of liquid metals on solids in stressed and unstressed states. The following corrosion action of liquid metals is described: the mechanisms of dissolution, non-isothermal and isothermal mass transfer, intercrystalline fracture, formation of compounds and solid solutions, effect of impurities in liquid metals, etc. The changes occurring in the mechanical properties of solid metals under the action of liquid metals during short duration tests and during long-term strength, creep and fatigue tests are also described. Adsorptive, corrosive and diffusive effects of liquid metals on solids in a stressed state are discussed. In Part II, the mechanism of the reaction of liquid metals on solids in a stressed state, is discussed in continuity with Part I.			

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DEFORMATION AND FRACTURE IN LIQUID METALS

The effect of a liquid metal medium on a solid metal in an unstressed state has been discussed in the first section of this book. Let us now examine the effect of the medium on a metal in a stressed state. The influence of the liquid metal in this case is characterized by a number of peculiarities and is more diversified.

In the deformation and fracture process of the metal, the medium exerts a corrosive effect on it in the same manner as in the unstressed state, however, it is of a qualitatively different nature. For example, an abrupt decrease in strength and ductility of the solid metal in liquid metal may occur even for a relatively weak corrosion process. In some cases materials characterized by low corrosion rates undergo a greater reduction in strength and ductility in a liquid metal medium than those which are less corrosion-resistant.

Although the corrosion rate of stressed metals increases, the effect of stress should not be considered as a factor promoting the increase of the corrosion process. In some instances fracture occurs with a slight increase in the overall corrosion rate of the metal whereas in an inactive medium under those same loading conditions its strength is much greater.

Unusual effects which are caused by the adsorptive influence of the medium can be observed in the deformation of a solid metal in the liquid.

This type of liquid metal effect occurs specifically in a stressed state and is not observed in the absence of stresses. In principle the adsorptive effect differs from the corrosive effect. It occurs in the free surface energy of the solid metal in contact with the liquid is smaller than that in the inactive medium. Reduction in the surface energy of the deformed metal eases the plastic deformation process, decreases strength and ductility of the solid metal and promotes some other effects. Unlike corrosion, the adsorption action of a liquid metal medium is reversible. It disappears after deformed solid metal is separated from the liquid metal.

It should be noted that the adsorptive effect of the liquid metal on the solid metal may be associated with the adsorption of this process in the usual physico-chemical sense. In this case by adsorptive effect of a medium it is meant any change occurring in the mechanical properties of the metal as a result of a change in its free surface energy under the action of the medium.

The third type of liquid metal effect on a solid in the stressed state is the diffusive effect. It is associated with the penetration of atoms of the medium into the solid metal. It is characteristic that in this case, in the same manner as in the adsorptive effect, the surface layer of the metal does not show any damage to the structure. Metallographic analysis frequently fails to show diffusion through the selection of special corrosion agents. Even though the solid metal, judging by the change in its mechanical properties,

experienced the effect of the liquid metal medium, its microstructure remained the same.

One of the characteristic features of diffusion action in contrast to the adsorption is its irreversibility. Testing the specimen after removal of the medium indicates that its mechanical properties changed when compared with the original state.

The nature of the diffusive effect enables one to treat it as a separate type of action of the medium. Actually in this case the medium affects the deformation and fracture processes in the interior of the metal whereas adsorption and corrosion affect its surface.

In the study of the corrosion processes we included the formation of solid solutions by solid and liquid metal. In conformance with this classification the diffusive effect of the medium is another type of corrosion. However, when describing the deformation and fracture of metals the diffusion action should be correctly considered as an independent process. With this type of metal defect the dislocation of the entire surface layer is absent in contrast to other types of corrosive effect. Moreover, in many cases the concentration of dissolved metal due to diffusion is increased very slightly, for example by one thousandth per cent*.

Thus, the effect of liquid metal on a solid in the stressed state may be adsorptive, corrosive or diffusive. Consequently, one may also

*In these cases the diffusive effect appears together with the adsorptive effect (see Chapter 5).

indicate the adsorptive, corrosive and diffusive factors of influence of the medium. In the general case the influence of the liquid metal may be determined by the combination of all three factors. Under certain conditions only one of them can be the controlling factor. Since the basic external appearances of the effect upon the mechanical properties of solid metal are similar, it is difficult to determine the degree of the influence of each factor separately.

The first four chapters of the second portion of this book are devoted to mechanisms of liquid metal effects on solids which are observed under different mechanical tests. The phenomenology of the discussed effects is given here. The factors determining the influence of the medium are indicated in those chapters only where they are positively established.

In the chapter on the mechanism of the liquid metal effect the processes responsible for the adsorptive, corrosive and diffusive influence are described as well as the characteristic features of the action of each of these factors on the mechanical properties of the solid metal. The mechanisms of liquid metal effect on solids, which were described in the first four chapters are also explained in the chapter indicated above.

Chapter 1 - MECHANICAL PROPERTIES DURING BRIEF TESTS

a. General mechanisms for changing mechanical properties

Extensive investigations of the effect of liquid metals on single crystals of different metals under constant strain rate were carried out by Academician P. A. Rebinder and V. I. Likhtman and YE. D. Shchukin (Doctorate in Physico-Mathematical Sciences) at the Institute of Physical Chemistry of the Academy of Sciences of the USSR and at the Department of Colloidal Chemistry of the Moscow State University. Single crystals were grown by the method of zone crystallization. Tensile tests were carried out on cylindrical specimens with a diameter from 0.5 to 1 mm. A low melting metal was deposited on the surface of the specimens by chemical, electrolytic or mechanical means. It was shown that the action of the liquid metal does not depend on the manner of its deposition. The thickness of the coating was usually several microns. The influence of liquid metal is determined by the adsorption factor.

The corrosive effect of the liquid metal coating was excluded since its thickness was small and an extremely small amount of tested solid metal dissolved in it. Consequently, the change in the specimen dimension was negligible. In order to verify the validity of this assertion tensile tests of zinc single crystals were carried out in a bath with liquid tin saturated with zinc. The stress-strain curves obtained from this experiments and from the experiments of zinc specimen coated with tin were the same [186].

Experimental verification of the absence of the influence of volume diffusion on the observed effect was also obtained. For example, based on the measurement of electrical resistance of a zinc single crystal coated with mercury, the diffusion coefficient of mercury in zinc was determined. It was found that at room temperature it is about $3 \times 10^{-11} \text{ cm}^2/\text{sec}$ [187]. Since mercury affects the mechanical properties of zinc immediately after its deposition on the specimen, i.e. after several seconds, it is obvious that the effect was not caused by volume diffusion.

Fig. 72 shows the stress-strain curves of zinc specimens coated with tin [189]. It is evident that the surface layer exerts an influence on the mechanical properties of single crystals only when it is in the liquid state. At room temperature the stress-strain curves of the specimens with and without the coating practically coincide. The coated specimen is strengthened very slightly probably due to the thin coating film of tin. The mechanical properties of test specimens were significantly changed at temperatures insuring the melting of tin. In this case two types of stress-strain curves were observed. At a temperature of 250°C "true stress - relative elongation" curves of pure specimens and coated with liquid metal coincide up to the instant of failure of the coated specimen. The effect of the liquid metal in this case was expressed in the decrease of strength of the solid metal and particularly in the decrease of ductility. At temperatures 350 and 400°C another type of curve was observed.

In this case only the initial portion of the curves (region of elastic deformation) coincides. The action of the liquid metal causes not only the decrease of strength and relative elongation but also the decrease of yield point and coefficient of hardening. The similarity in both types of stress-strain curves was also observed when testing other single crystal specimens with liquid metal surface coating.

In many cases the mechanical properties of the solid metals were abruptly changed under the action of the liquid metal medium. This change is so great that a coated metal has qualitatively different mechanical properties than the pure metal [186]. High-ductile materials capable of elongating under tension by one hundred percent become brittle as a result of the effect of the liquid metal surface layer. In this case if the base metal fails locally with necking down, the coated metal fails without local deformation with a break in the shear plane [194].

The degree of liquid metal effect on the mechanical properties of single crystals depends on the orientation of the latter with respect to tensile force. Fig. 73 shows the dependence of true fracture stresses for zinc single crystals on the angle of inclination χ_1 between the basal plane and the specimen axis during fracture [188]. This Fig. also shows the results of testing specimens coated with mercury at room temperature and uncoated specimens which were fracture at a temperature of -196°C . It is evident that the orientation dependence of strength in zinc single crystal in both cases has the same character.

Values of normal and shear stresses during fracture also revealed an orientation dependence of deformable single crystals. Such a dependence for zinc single crystals, tensile tested with constant rate at the temperature of liquid nitrogen (-196°C) without a coating and at a temperature of 20°C with a mercury coating, is shown in Fig. 74 [189, 190]. Brittle fracture caused by lowering the temperature and by the action of the liquid metal is characterized by qualitatively similar mechanisms. E. D. Shchukin and V. I. Likhtman showed that with the increase in the angle between the basal plane, on which fracture occurs, and the specimen axis, the values of normal stress increase and the values of shear stress decrease. Such a change in stresses indicates that failure of single crystals occurs as a result of plastic deformation leading to the formation of fracture [189]. If the angle between the basal plane and the specimen axis is sufficiently great, i.e. at relatively great normal stresses, the brittle fracture on the slip plane which in the given case is also the shear plane, occurs in the earlier stages of the fracture development. However, if the indicated angle is small and hence the normal stresses are low, then fracture occurs at a later stage of fracture development subsequent to great plastic deformation. The decrease in the ability of zinc single crystals to resist plastic deformation with the increase of the angle between basal plane and the specimen axis can be judged by the values of limiting crystallographic shear which are given in Table 33.

Data in Table 33 indicate that under the conditions of brittle fracture the magnitude of the limiting crystallographic shear steadily decreases with the increase of the angle between basal plane and specimen axis. However, different results were observed during tensile tests of zinc single crystals without surface coating at room temperature, i.e. when the metal is ductile. In this case the crystallographic magnitude does not decrease with the increase of α° , on the contrary it increases [191]. Consequently, the orientation dependence of the limiting crystallographic shear qualitatively varies as a result of deposition of liquid metal layer on the surface of a single crystal.

The mechanisms of the influence of liquid metals on mechanical properties of zinc single crystals indicated above are characteristic not only for this metal. Experiments showed that cadmium single crystals coated with liquid tin [192, 186], and gallium [193], as well as tin single crystals coated with mercury [194-196] and gallium [197] behave similarly to the above. It was found that the mechanisms of the influence of different surface active liquid metals (tin [186, 192], mercury [191, 195, 198] and gallium [193, 199]) on zinc single crystals were identical.

Not only single crystals but also polycrystals are subjected to the influence of liquid metals during constant strain rate. It has been established by testing polycrystalline specimens that the action of liquid metals in this case also leads to the decrease of strength and ductility of the material. As in the testing of single crystals, two types of

variation of stress-strain curves of the polycrystalline metal with surface coating from the initial curve of that same metal without coating were observed. In some instances the curves coincide up to the fracture of the coated specimen, which occurs at a smaller magnitude of tensile strength and relative elongation than that of the uncoated specimen. In other instances, less common, the entire curve of the coated specimen, with the exception of the elastic strain portion, is located below the curve for the pure specimen. A special case of the curve of the first type are the curves having only an elastic portion, i.e. those when the specimen in the liquid metal is fractured during strain lower than the elastic limit.

Fig. 75 shows the stress-strain curves of 30KhGSA steel at a temperature of 500° C in air and in liquid metals: Bi, eutectic Pb-Bi and alloy Pb-Sn [200]. It is evident that all the liquid metal agents caused the decreased in the true strength, tensile strength, relative elongation and coefficient of steel hardening. The degree of influence of various agents is different. The changes in the stress-strain curves of 30KhGSA steel refer to the second type of classification accepted above.

The fracture of alloy EI437A during a constant rate tensile test in the following liquid metals: Sn, alloy Pb - 40% Sn, Pb, Bi and the eutectic alloy Pb-Bi occurred in the elastic region, i.e. the stress-strain curves in this case also agree with the second type. It should be noted that an extremely high liquid metal influence on the mechanical properties of the alloy was observed in these experiments [201].

Thus, for example, in air medium at a temperature of 700°C alloy EI437A has a strength of 75 kg/mm^2 and yield point of 48.5 kg/mm^2 ; contact with eutectic Pb-Bi caused its fracture under a stress of 25 kg/mm^2 .

Let us cite some more examples characterizing the interaction of liquid metals on solids under the constant rate tensile tests. These examples also indicate the wide range of materials subjected to the influence of liquid metals.

Miller disclosed [202] the significant reduction in strength and ductility of 70/30 and 60/40 brasses as a result of contact with liquid mercury, tin and tin-lead solder (50/50). With the effect of mercury at room temperature the strength of brass decreased by a factor of three. In liquid tin at a temperature of 260°C the decrease in the strength of 70/30 brass was 18% and 60/40 brass 28%. The strength of these materials in a tin-lead alloy at 220°C decreased approximately as much as the above. At a temperature of 350°C the decrease in strength of 70/30 brass in liquid lead reached 40% and in tin 33%.

The plastic properties of the materials decreased even to a greater extent. Thus, the relative elongation of 70/30 brass in liquid tin at a temperature of 260°C was 2.5% whereas in air at that same temperature it was 27.5%. The limiting values of relative elongation obtained in the testing of this material in mercury and in air were 3 and 38.8% respectively. In the case of the action on brass solder the corresponding values of relative elongations are the following: 2 and 28%.

Austen [203] carried out tensile tests with constant rate deformation for different steels and other materials in contact with tin-lead (60/40) solder. He established a significant decrease in strength and ductility in the liquid metal of pearlite steels as well as stainless ferrites and austenites. Fracture in certain materials, for example, low-alloy nickel chromium vanadium steel occurred in the elastic region at a temperature of 290° C. Pure metals: Fe, Ni and Cu were subjected to a significantly lower influence of the medium. Stress-strain curve of materials in the liquid metal usually coincide with their stress-strain curve in air, but fractured at lower values of stress-strain and relative elongation.

S. T. Kishkin, V. V. Nikolenko and S. I. Ratner carried out tensile tests for 30KhGSA, 18KhNVA and 40KhNMA steels at a high temperature in the medium of liquid solders [204]. The influence of solders was investigated by two methods. In the test by the first method the specimen coated with solder was placed in the furnace and tensile tested at a temperature insuring the melting of solder. In the test by the second method the specimen was loaded to a certain strain, after which its surface was coated with solder. If during the application of solder (about 3 minutes) the specimen would not fracture then it was loaded to a strain exceeding the initial by 5 kg/mm^2 . With this strain, the specimen surface was also soldered, etc. These operations were carried out until the specimen fractured. Results of testing by two methods were found to be the same. Under the action of tin-lead solder

(61% Sn, 39% Pb) the fracture of steels occurred at a tensile stress of 85-95 kg/mm², which corresponded to the elastic region for some steels and to the plastic region for others. However, the strength and ductility in the second group of steels was also lower than in air. The change in mechanical properties of steels was also caused by lead-silver solder PSP-3 (97.5% Pb; 2.5% Ag), but its influence was somewhat lower than that of tin-lead. In Ref. [204] it was shown that solders in the solid state practically do not exert an influence on the strength and plastic properties of steels.

Tensile tests for a great number of different materials were carried out in the medium of liquid metals by Ya. M. Potak and I. M. Shcheglov [205, 206]. They and other investigators established that the strongest effect of liquid metal coating was exerted on the plastic properties of metals and alloys: relative elongation and reduction in area of certain materials decreased more than tenfold whereas the strength in this case decreased twofold. However, not all the materials display the influence of surface coatings. For example, the mechanical properties of copper in tin-lead solder did not change at a temperature of 270-280° C. It was found that aluminum alloys of the AMTs and Al9 type were not susceptible to the action of this coating at a temperature of 270-280° C. It should be noted that high tempered 30KhGSA steel was subjected to a significant influence of the tin-lead coating at that same temperature. Thus, the action of liquid metals is selective. The same melted metal exerts an influence on the deformation and fracture of some solid metals and not on others.

The effect of liquid metals on the mechanical properties of solids occurs not only during constant rate tensile tests but also with other types of mechanical coatings. Many investigators observed the effects of a medium in a bending test of the specimen. It was established that fracture occurred with decreased strength and ductility of low-alloy pearlite and high-alloy austenite steels during bending tests of the specimens in contact with tin-lead solder (63% Sn and 37% Pb) and with babbitt (tin-antimony-copper alloy) [207]. The influence of liquid Zn, Sn, and Sb on the mechanical properties of steel during bending was also described [208]. The influence of mercury coating in copper specimens during that same type of testing was noted in Ref. [209].

In references cited above it was shown that the fracture of specimens coated with liquid metal occurred in a number of cases with an insignificantly low angle of bending, i.e. the influence of the medium, in the same manner as during tensile testing, causes the metal to abruptly loses its ductility. It was established that liquid metal exert an influence only when they are deposited on the stressed side of the specimen [207, 210]. If there is a coating on both sides, then there will be no cracks on the compressive side. Consequently, premature fracture in the liquid metal environment is caused only by tensile stresses.

G. F. Kosogov and V. I. Likhtman [211] compared the influence of liquid tin on the mechanical properties of steel of type St. 7 during axial tensile and torsional tests at a temperature of 350° C. The data obtained by them (Table 34) indicates that the action of liquid metal appeared only during stress.

This result is probably associated with lower values of normal stresses during torsion [212].

Many investigators have noted the intensification in the influence of liquid metals on the deformed solid metal with the increase in strength of the latter. For example, authors of references [204-206] have observed a significant decrease in mechanical properties of 30KhGSA steel in contact with tin-lead solder and tin when it had an initial strength of about 170 kg/mm², and no change (or a slight change) of properties in the steel with a strength of 60 to 70 kg/mm². 30KhGSA steel having a strength of about 120 kg/mm² in air is subjected to lesser influence of liquid metal than that same steel with a higher strength. Table 35 shows the corresponding data obtained in references [205, 206].

The dependence between ratio of strength of aluminum alloys in liquid mercury to air $\frac{\sigma_B(\text{liq. mer.})}{\sigma_B(\text{air})}$ on the magnitude of initial strength $\sigma_B(\text{air})$ given in Fig. 76 is plotted according to the data in Ref. [213]. Despite the noticeable scatter in the graph, it is evident that with the increase of initial strength of aluminum alloys their susceptibility to the action of liquid mercury increases. Thus, alloys having a strength of 45 to 70 kg/mm² in air, retain only 10-20% of the initial value of strength in the liquid metal. However, alloys having a strength of 20-35 kg/mm² in air either are not subjected at all to the influence of the liquid metal or undergo a slight (about 10%) decrease in strength.

It should be indicated that the dependence of the influence of liquid metal on the strength level of the solid metal is not always apparent. For example, in Ref. [207] it has been shown that chromium-nickel steels have about the same strength in air but differ in a medium of melted solder. This observation as well as the dependence stated in Fig. 76 enables one to make the conclusion that the increase in the effect of liquid metal on the deformed solid metal with the increase of its strength is only a trend. In other words a high level of initial strength is only one of the many factors favoring the increased action of the liquid metal.

Investigation of the microstructure of fractured specimens in liquid metal has shown that polycrystalline metals are usually fractured at the grain boundaries. This type of fracture is observed even in those cases, when testing in air the cracks propagate across the grain [204-206, 214]. Intercrystalline fracture was also found in those metals which are subjected to a strong influence of the medium, being in the single crystalline state.

Investigation of the generation of cracks in polycrystalline pure metals during their deformation has been carried out by S. M. Zanozina and E. D. Shchukin [215]. A special attachment was made to the metal microscope which enabled one to deform the flat specimens smoothly by stressing it. The deformation process was observed through the microscope.

It was established that cracks are formed in the specimens with a liquid metal coating and increase with increased deformation mainly at the grain boundaries. This type of fracture was observed in zinc and cadmium with a gallium coating. Sometimes the cracks are propagated at the grain but they are significantly less. A mixed type of fracture, but mostly intercrystalline, occurs in zinc coated with mercury.

E.D. Shchukin and Z. M. Zanozina were the first who showed that fracture begins at the boundaries of those grains in which the slip lines appear first.

Nichols and Rostoker determined the mechanical properties of different coarse-grained materials during local deposition of liquid metal on the surface of specimens [216].

The results of their investigation given in Table 36 showed that during the deposition of liquid metal only at the grains the effect is either absent or is significantly lower than during the deposition of the metal at the grain boundaries. For example, the relative elongation of silicide steel decreased from 20 to 7% in the deposition of lithium at the grain and to 1.6% in the deposition of lithium at the grain boundary. 70/30 brass did not undergo any changes in strength and ductility in the deposition of mercury at the grain but underwent a decrease in strength from 17.7 to 6.1 kg/mm² and relative elongation from 42 to 8% in the deposition of liquid metal at the grain boundaries.

It is evident from Table 36 that although the influence of the liquid metal during wetting of the grain boundaries is greater than during wetting of the grain body, it is weaker than when wetting large areas of the specimen surface. This is apparently associated with the great probability of the most stressed and the most unfavorably oriented grain boundaries falling into the wetted area.

The results of experiments carried out on bicrystals confirm the extremely significant dependence of the wetted grain boundary by liquid metal [8]. Copper bicrystalline specimens wetted with bismuth were tested at a strain rate of 0.016 min^{-1} . It was shown that maximum embrittlement by liquid metal occurred when grain boundary was transverse to the axis of loading. When decreasing the angle between them from 90° to 0° the embrittlement steadily decreased and the strength and ductility of bicrystalline specimens approach the strength and ductility of single crystalline specimens (Table 37).

b. Influence of temperature

The temperature refers to a number of factors exerting a significant effect on the magnitude of change in mechanical properties of solid metals under the action of liquid metals. Moreover, at a certain temperature this action does not appear at all [194, 346].

Experiments carried out on single crystals coated with a thin layer of liquid metal showed that their strength and ductility are usually restored with the increase in temperature and beginning with a certain value the mechanical properties of coated and uncoated specimens are the same. Fig. 77 shows the dependence of true strength and elongation during fracture on the temperature for pure tin single crystals and coated with mercury [194, 217]. It is evident that the effect of mercury occurred beginning with the melting point. In the range -40 to 20°C the specimens coated with mercury are fractured at low values about the same as those of relative elongation. At a higher temperature the ductility of these specimens is increased and beginning with 20°C it becomes the same as in the uncoated specimens. If one judges the influence of temperature according to the change in true strength then the effect of liquid metal steadily decreases with the increase in temperature from -40 to $+20^{\circ}\text{C}$. It should be emphasized that the disappearance of the influence of the liquid metal during the increase in temperature was not caused by its evaporation since the effect was reversible, i.e. it was restored when the specimen was cooled.

It was established that the effect of liquid mercury on the zinc single crystals is characterized by that same temperature dependence as the effect of mercury on tin described above [195, 218, 219]. The influence of liquid metal on zinc disappeared at a temperature higher than 150°C . The characteristic properties of this material were restored in the temperature range of $110 - 160^{\circ}\text{C}$, while the nature of fracture

of single crystals changed from brittle, with mirror-like cleavage at the basal plane, to ductile at an elongation up to several hundredths of percent, with pronounced local deformation.

Experiments with zinc and cadmium single crystals with a tin surface coating showed a different temperature dependence of influence of liquid metal medium. In this case with the increase in temperature the influence of liquid metal on strength and ductility of single crystals steadily increased [186, 192]. The degree of this influence can be judged by the zinc stress-strain curves given in Fig. 72.

Experiments of polycrystalline metals in a liquid metal medium at different temperatures have shown that the mechanism of temperature influence is the same as in the experiments with single crystals.

G. F. Kosogov and V. I. Likhtman investigated the temperature dependence of the effect of liquid tin and lead on the strength and ductility when stressing steels containing from 0.05 to 1.10% carbon at a rate of 1.25 mm/min [211]. They established that liquid metals cause a decrease in strength and ductility of steels within a given temperature range above the melting point of the medium. The experiments show that the decrease of the strength and ductility have a maximum within a given temperature region depending on the concentration of carbon in steel (Fig. 78). Consequently, the temperature range in which the effect of liquid metal is exerted increases, with 0.05 carbon content the influence of tin was observed in a temperature range between 200-400° C, and in steel with 1.08% carbon the lower range boundary is the same and the upper reaches 600° C.

V. G. Markov [214] observed a similar dependence of influence of liquid tin on the mechanical properties of steel upon the testing temperature.

The experimental results of mechanical properties at a strain rate of 16% of Armco-iron and steels at different temperatures are given in Ref. [220]. The specimens were coated with liquid Cd, Zn and Sn. It was established that the influence of liquid metals on the Armco-iron, carbon and low-alloy steels (St. 20, St. 45, 40KhNMA and 30KhGSA) is exerted within a certain temperature range, which is limited to below the melting point of the coating; the upper temperature boundary depends on the type of steel and its heat treatment and differs for various liquid metal coatings. Austenitic steels 1Kh18N9T and EI878 with zinc coating in contrast to the above indicated steels steadily increase the effect of liquid metal with increase in temperature (Fig. 79).

Continuous increase of the effect of liquid metal with the increase in temperature was observed by Ya. M. Potak and I. M. Shcheglakov [205, 206]. Table 38 shows the results for steels 30KhGSA and EI388 tested in liquid tin by the above cited authors. It is evident that 30KhGSA steel after hardening and tempering with the increase in test temperature in liquid tin from 270 - 280 to 400° C becomes a completely brittle material, breaking without plastic deformation, whereas at 400° C in air it has a relative elongation of 13.2% and relative reduction in area of 36.7%. 30KhGSA steel, after annealing, is not subjected to the influence of tin at 270 - 280° C, i.e. at a temperature somewhat higher than the melting point

of the coating. The increase of the testing temperature led to a significant decrease in its strength and ductility, so that at 500° C the annealed 30KhGSA steel with a tin coating became a brittle material (relative elongation of 2%, and relative reduction in area of 6%). Similar results for a continuous increase of the influence of liquid metal on the strength and plastic properties of materials with the increase of testing temperature were also obtained in references [207, 208].

Thus, the temperature dependence of the influence of liquid metals on the mechanical properties of single and polycrystalline metals is the same and appears in two forms. In one instance the effect has low and high temperature boundaries, and in the other only a low temperature boundary exists, which continuously increases with increase in temperature.

c. Influence of the deformation rate

The deformation rate exerts a considerable influence on the effect of liquid metals on solids. This influence was detected when testing single and polycrystalline metals.

Fig. 80 shows the change in true strength and limiting relative elongation for tin single crystals during a tensile test with different deformation rates [193, 217]. It is evident that by changing the rate of strain both an abrupt embrittlement of specimens coated with mercury can be obtained or the influence of mercury can be eliminated completely. It follows from Fig. 80 that the maximum effect of liquid metal on the tin single crystal at room temperature was observed for the largest

deformation rate, higher than $10^6\%/min$. The reduction of the deformation rate leads to the decrease of the effect and at a rate of less than $10^3-10^4\%/min$ the effect is absent.

The tests of polycrystalline specimens have shown a more complex nature of the influence of the deformation rate. In certain papers it was also observed, as in the case of single crystals, a weakening or, in the extreme case, a disappearance of the effect of liquid metal during the decrease of the deformation rate. Fig. 81 shows the stress-strain curves of specimens of St. 20 with two strain rates - 10 and 0.055 mm/min, which were obtained by M. I. Chayevskii and V. I. Likhtman [221, 222]. The experiments were carried out on cylindrical specimens with a working area of 10 mm in diameter and 40 mm long. The test temperature was $400^\circ C$. The influence of two liquid metal melts, eutectic alloys Pb-Bi and Pb-Sn, was investigated. It is evident from Fig. 81 that with a deformation rate of 10 mm/min the carbon steel undergoes a decrease in strength and ductility under the action of both melts (curves 1, 3, 5). With a lower deformation rate (0.055 mm/min) the mechanical properties of steel in air and in the indicated liquid metals are the same.

An analogous action of the deformation rate on the influence of a liquid metal medium was also observed in experiments with 20Kh steel [223]. The tensile test for the specimens prepared from this steel was carried out with that same deformation as in the specimens of St. 20, i.e. 10 and 0.055 mm/min. The test temperatures were 400, 450, 500 and $600^\circ C$.

An alloy containing 59.5% Sn, 36.7% Pb and 3.8% Al was used as a liquid metal medium and the specimens were elongated in a liquid metal bath. It has been established that with a deformation rate of 10 mm/min the effect of the melt, expressed in the abrupt loss of steel capability to plastic deformation, occurs only at a temperature of 400° C. The decrease of the deformation rate to 0.055 mm/min led to complete restoration of mechanical properties of steel in contact with liquid metal to the initial level.

An analogous action of the deformation rate on the effect of liquid indium on an aluminum alloy was observed by Rostoker, McCaughey and Markus [8].

In other studies the influence of the deformation rate on the described effect was directly contrary to that observed in the above investigations. It has been indicated that the increase of the deformation rate of the materials leads to the weakening of the effect of liquid metal environment. Ya. M. Potak and I. M. Shcheglakov investigated the behavior of 30KhGSA steel under static and dynamic bending [205, 206]. The test was carried out on a cylindrical specimens (19 mm in diameter) with a circumferential notch at a temperature of 300° C. One set of specimens was tested without a surface coating and the other with a tin coating. The rate of the static bending was 1.5 mm/min and dynamic bending was 3.6×10^5 mm/min. The steel was tested with a high and an average strength level. Experimental results are given in Table 39.

It is evident from the Table that the work of rupture of steel specimens under static bending decreased under the action of liquid tin by more than one order of magnitude. Rapid loading of specimen removed the detrimental influence of liquid metal surface film almost completely.

Greenwood investigated the mechanical properties of copper at various strain rates [224]. Specimens coated with mercury were used. The results are given in Table 40. The Table shows the mechanical properties of uncoated copper only at a strain rate of 40%/hr, however tests were also carried out at other rates. The experiments show that in the range of investigated deformation rates the mechanical properties of uncoated copper specimens remain the same. Based on data in Table 40 one can conclude the significant weakening of the effect of liquid mercury on copper with the increase of the deformation rate from 0.2 to 1000%/hr. The data in Table 40 also show that the nature of the influence of the deformation rate on the effect of liquid mercury is the same for copper with coarse and fine grains.

The weakening of the effect of liquid solders on the mechanical properties of steels during bending with an increased load rate was noted in Ref. [207].

The experimental results stated above enabled one to indicate the two boundaries of liquid metal effect [219, 345] . Evidently, at a constant temperature the influence of liquid metals can be observed within a given range of deformation rates. The effect does not appear for lower and higher values than those determined for deformation rates.

The correlation between the influence of the deformation rate (lower boundary) and the temperature (upper boundary) on the action of liquid metals should be noted. Thus, the increase in test temperature may lead to a transfer of a boundary developing the effect into the region of higher strain rates or to its disappearance. A similar increase in the deformation rate may cause a substantial rise in the threshold temperature of induced brittleness. The relationship between the temperature and strain rate based on the tests of aluminum alloy wetted with a liquid mercury containing 3% zinc [8] is found in the form of

$$T = A \ln v + B, \quad (148)$$

where T is the temperature; v is the deformation rate; A and B are the constants. Equation (148) is obtained by connecting the points on the "temperature-strain rate" graph which corresponds to similar magnitude of relative elongation of specimens. In the given case the corresponding constants of the tested metal were such that the metal possessed the same ductility.

It should be noted that the relationship between the temperature of brittle transition and strain rate was first established when testing metals in an inactive medium by F. V. Vitman and V. A. Stepanov [343]. Its applicability for interaction conditions of adsorptive-active liquid metal was established by V. I. Likhtman and E. D. Shchukin [219].

d. Influence of grain size

The same metal but with a different grain size is subjected to the effect of the liquid metal environment to a varying degree. In all investigations, devoted to the study of the influence of grain size, an unambiguous result was obtained. It was established that with the increase in the mean grain diameter the strength of a solid metal in contact with a liquid metal is decreased.

This was concluded, for example, from the results presented above for tensile test with various deformation rates of copper specimens coated with mercury. It follows from Table 40 that the strength and relative elongation of specimens with a mean grain diameter of 0.1 mm is lower than that of specimens with a mean grain diameter of 0.03 mm in all rates of strain employed.

The mechanical properties of annealed LS59-1 brass with a grain diameter of 50, 220, 280 microns were investigated in Ref. [225]. The test was carried out by elongating the specimens at a constant deformation rate of 0.03 mm/sec. One set of specimens was tested with mercury coating and the other without a coating. They were tested at room temperature. The results obtained indicate that with an increase in grain size the strength of pure specimens and those with a liquid metal surface film decreased. However the degree of decrease in their strength is not the same: under the action of liquid mercury the decrease in brass strength with the increase in grain size occurs more intensively.

For example, with a grain diameter of 220 microns the strength of brass in mercury is 31% lower than the strength in air, and with a grain diameter of 280 microns it is 40% lower.

It has been established by bending tests of steel specimens in contact with molten tin-lead solder that the effect of liquid metal is also reduced with the decrease in grain size [207].

A functional relationship between the true tensile strength in a liquid metal medium and mean grain diameter of the metal being tested was found. Fig. 82 shows the dependence between these magnitudes for 70/30 brass at room temperature, obtained in Ref. [226]. In accordance with the graph the following expression may be written

$$S_k = S_0 + Kd^{-1/2}, \quad (149)$$

where S_k is the true tensile strength of brass with a mercury coating; d is the mean diameter of grain; S_0 and K are the constants.

Similar dependence were also obtained when testing low-carbon steel in lithium at a temperature of 250° C [226], cadmium in gallium at 25° C [227] and copper in mercury at 25° C [228] and in lithium at 205° C [8]. It should be noted that equation (149) is frequently not obtained when testing those same materials in air. The reason is that significant plastic deformation precedes the fracture of metal in air. When the fracture of specimens which are not in contact with liquid metal is brittle the relationship between the fracture stress and grain diameter is also described by equation (149) [227, 229, 230].

The relationship (149) is valid not only for true strength but also for the yield point [8] and limit of proportionality [227]. It is evident from Fig. 83, which shows the results of constant rate tensile tests carried out for 70/30 brass coated with mercury, that the constant K in equation (149) is lower for the yield point than for true tensile strength whereas the magnitude S_0 remains the same. The difference in constants K indicates that with the decrease in grain size the difference in true tensile strength and yield point is increased, i.e. the smaller the grain diameter the greater plastic deformation preceding the fracture of the specimen.

Nichols and Rostoker investigated the stress necessary to initiate cracking or to propagate cracking in 70/30 brass wetted with mercury at room temperature as a function of the mean grain size. The stress necessary for crack initiation was determined by testing the specimens which had been pre-cracked across a portion of the test-section. The re-initiation stress was computed on the basis of measured tensile force and the residual uncracked cross section. The experiments have shown that the stress necessary for crack initiation is higher than the stress necessary for its propagation during which the difference between them is greater the lower the linear dimension of the grain. The relationship between each of these characteristic stresses and the inverse square root of the mean grain diameter was found to be linear similarly to equation (149).

The grain size of solid metals also affects the temperature at which the transition from brittle to ductile behavior occurs (see Chapter I). The tensile elongation as a function of temperature for annealed 70/30 brass of various grain sizes was investigated in Ref. [231]. It has been established that the embrittlement in brass by liquid mercury is temperature dependent and that the temperature is governed by the grain size. Fig. 84 shows that the correlation between transition from brittle to ductile behavior and the logarithm of the mean grain diameter is linear.

e. Influence of stress concentrators

The experimental results of the influence of notched type stress concentrators on the effect of liquid metals on solid metals in the deformation process are discrepant.

The influence of stress concentrators in the form of a circular hole in the middle portion of flat specimen on the mechanical properties of L68 brass in tension was investigated in Ref. [232]. The specimens had a working area 4 mm wide, 14 mm long and 1 mm thick. The hole was 0.8 mm in diameter. The specimens were tested without and with mercury coating at room temperature. Table 41 shows the experimental results. The Table also includes values of effective coefficients α_{eff} which were calculated as a ratio of specimen's strength with stress concentrator to the strength of flat specimen.

The relative elongation in this case is an arbitrary magnitude. It is calculated as a ratio of elongation of the working area of the notched specimen to its initial elongation.

It is evident from data in Table 41 that a stress concentration at the circular hole in the flat specimen appeared when testing in air but when testing in liquid mercury its influence is almost absent. Consequently the degree of mercury effect on the strength and ductility of specimens with stress concentrators is lower than on the strength and ductility of flat specimens. The notch action also did not appear when testing flat specimens of L62 brass with notch in a form of circular hole, when their surface was coated with mercury [233] ,

Results similar to those stated above were also obtained during tensile tests of flat specimens with notches on the sides [8] . Aluminum base alloy type 2024-T4 was used as a test specimen and mercuric amalgam as a liquid metal. It is evident from Fig. 85 that the fracture stress is practically the same in flat specimens with grooves of different radii of curvature up to 0.1 mm.

There are also papers in which the intensification of liquid metal effect on specimens with stress concentrators was compared to specimens without concentrators. For example, authors of Ref. [220] tested specimens of steel 40KhNMA with a circular notch 1 mm deep and 0.2 mm in radius. They observed a sudden drop in the strength and ductility in cadmium coated specimens in the range 320-480° C.

The strength at 350° C is only half that of the specimens without coating. At the same time the flat specimens under the action of cadmium experience only a slight reduction in strength.

It has been shown in Ref. [221] that the specimens of St. 20, which were tensile tested at a constant rate in a melt of eutectic Pb-Sn, revealed increased ductility if the working parts of the specimen are ground and noticeably lesser if marks from the lathe machining are not removed.

Ya. M. Potak indicates almost a sixfold reduction in strength of 30KhGSA steel under the action of tin-lead solder during a bending test of notched specimens [206]. Tensile test of flat specimens under such conditions showed that their strength decreased by 10%. Although a bending test in a liquid metal is more rigid since the surface layer of the specimen is under maximum stress nevertheless the significant difference in the effect during tension and bending was apparently due mainly to the presence of the notch in the bending specimens.

Thus, the data available at the present time on the influence of stress concentrators on the effect of liquid metal on solid under the conditions of deformation and failure still do not enable to explain the general mechanisms. Based on the published data it is possible to conclude that the presence of stress concentrators either has not effect on the strength and ductility of the material in a liquid metal medium or leads to the increase of effect of the medium.

Based also on the general presentations one can expect that with a sufficiently developed dissolution process in the liquid metal the influence of the medium will lead to the decrease of action of rather sharp notches. On the other hand taking into account that the increase of stresses in the notch should intensify the influence of the medium the presence of a contrary action of stress concentrators under specific conditions should be considered possible.

f. Influence of cold-hardening

Preliminary plastic deformation of metal leads to its strengthening with subsequent deformation in liquid metal medium as well as in air. The degree of liquid metal influence can be both weaker and stronger in the cold-hardened material than in the starting material.

Table 42 shows the results of tensile tests of zinc single crystals subjected first to plastic deformation [189, 191]. Cold-hardening was carried by straining the specimens at room temperature. Subsequently one group of specimens was tensile tested at a temperature of -185°C and the other at $+20^{\circ}\text{C}$. The specimens of the first group were tested without surface coating and the specimens of the second group with mercury coating. Failure in both groups occurred at the basal plane and was brittle. Table 42 includes also the values of normal fracture stresses which enables one to compare the nature of strengthening of zinc single crystals under two types of brittle failure indicated above.

It follows from the Table that cold-hardening leads to the strengthening of single crystals which are pure and subjected to the influence of liquid metal. In this case the degree of strengthening of both single crystals under similar cold-hardening is about the same.

The testing of polycrystalline metals showed that they also develop a capacity of strengthening in liquid metal medium as a result of cold hardening. It has been established, for example, that such a strengthening is shown by an annealed L62 brass when tested in liquid mercury [234]. The test was carried out on cylindrical specimens with a working area 1 mm in diameter. Cold-hardening was set by tension at room temperature with a rate of 1.85 mm/min up to different magnitude of residual deformation (to 40% of residual elongation). Further testing of specimens was carried out also by tension at room temperature. It is evident from the experimental results given in Fig. 36 that cold-hardening leads to increase in strength and yield point and decrease of relative elongation and relative reduction in area of brass both in air and in mercury. However in all cases the strength and ductility characteristics of brass are substantially lower in liquid metal than in air. It should be noted that the yield points become almost equal to the strength of brass when testing in air after preliminary tension to 27% whereas when testing in liquid mercury they approach 8% already after tension. From a strength comparison in mercury and in air of the cold-hardened and starting material it should be concluded that the effect of liquid metal is lower on cold-hardened material.

A similar conclusion was made in Ref. [8] based on the determination of elongation during rupture in air and in mercury of a preliminarily cold-hardened aluminum alloy.

In addition to the data presented above there are investigations in which an increase of liquid metal effect on the solid metal subjected to preliminary plastic deformation was observed.

Fig. 87 shows the results of tensile tests carried out for 70/30 brass coated with mercury at a constant deformation after cold hardening [228]. It is evident that the specimens with a mean grain diameter of 0.032 mm undergo a reduction in true tensile strength for all values of preliminary plastic deformation. The specimens with a mean grain diameter of 0.08 mm after preliminary deformation to about 20% are strengthened and become soft at higher deformation. The specimens with a grain diameter of 0.16 mm and higher are strengthened after cold-hardening.

Experimental results on the influence of preliminary plastic deformation can be understood if one takes into consideration in this case the action of the following two factors. First, during cold hardening, an increase of material strength occurs and this should intensify the effect of the liquid metal. Second, cold-hardening causes grinding of structural components (grains, sub-grains, block structures) of solid metal which weakens the effect. Depending on the degree of influence of each of these factors the final effect is determined in each specific experiment. It is evident that for sufficiently fine grain in the tested metal the action of the first factor would be prevalent and cold-hardening will

intensify the influence of the liquid metal medium. A more effective action of the second factor should be expected in metals with relatively coarse grain and single crystals and consequently the weakening influence of the medium with the increase of degree of cold-hardening. The experimental results described above are in agreement with this explanation.

g. Influence of thermal and thermomechanical treatment

The degree of influence of the liquid metal medium on the deformed material depends on the thermal and thermomechanical treatment. This influence is determined to a considerable degree by the strength level and grain size acquired by the materials as a result of the treatment. However the action of thermal and thermomechanical treatment is also associated with certain peculiarities of the structural state of the material.

V. G. Markov investigated the effect of liquid tin on pearlite chromemolybdenum vanadium steel subjected to tempering at various temperature [214]. In all instances hardening was carried out at 990° C, and tempering at 270, 370, 470, 570, 670 and 770° C; the duration of tempering at each temperature was 1.5 hr. The specimens were made from steel billets, subjected to the indicated conditions of thermal treatment, with a cylindrical working area 6 mm in diameter. Subsequently the specimens were tensile tested at a rate of 1.25 mm/min.

The experiments were carried out in a bath with liquid tin and in air at a temperature of 250-650° C.

It has been established that the steel after low and mean tempering (at a temperature of 270-470° C) was affected the greatest by liquid metal. The specimens subjected to such a thermal treatment undergo brittle fracture without plastic deformation and their strength is lower than the yield point in air by a factor of 1.5-2. The specimens tempered at 570° C undergo fracture in tin after certain plastic deformation and there is a discontinuity on the stress-strain curve in the region of uniform deformation. Tempering at 670° C caused further weakening of tin influence on steel. In this case the yield points, strength and uniform elongation of the specimens tested in air and in tin are the same. The influence of liquid metal caused only the decrease of concentrated elongation. The specimens subjected to tempering at 770° C are not affected by the liquid metal medium.

Thus, the increase of a tempering temperature decreased liquid metal effect on the mechanical properties of pearlite steel. The weakening of the effect in this case is caused apparently by the decrease in strength of steel. Thus, strength in air changes continuously with about 130 kg/mm² after tempering at 270° C to 55 kg/mm² after tempering at 670° C.

Similar mechanisms for the thermal treatment effect of 30KhGSA steel on the magnitude of liquid tin and tin-lead solder influence have been established in references [204-206]. The results are

discussed above (see Table 35). It was noted in Ref. [235] that high temperature tempering of pearlite chrome-nickel and carbon steels decreased their susceptibility to melted solder effects.

Authors of Ref. [213] investigated the influence of mercury at room temperature on the mechanical properties of precipitation-hardened aluminum alloys as a function of the duration of aging. Fig. 88 shows the experimental results of an aluminum alloy with 4.5% Cu, 0.6% Mn and 1.5% Mg. It is evident that the increase in aging duration, followed by strengthening in air, caused an abrupt decrease of its strength in a liquid mercury medium. It is interesting that a slight alloy strengthening in the beginning of the aging process is caused by a strong influence of liquid metal. This indicates the dependence of the effect of the liquid metal medium on the structural state of the material.

A somewhat different influence of the liquid metal (mercury with 2% Na) is observed when aging Cu alloy with 2% Be [236, 237]. It follows from Fig. 89 that testing an alloy in liquid metal does not affect (qualitatively) the influence of aging on its yield point. In this case the usual strengthening stages and subsequently softening (with the increase of soaking) associated with the over-aging of alloy were observed. The influence of liquid metal on the relative elongation of the material was similar to the influence on the strength established in Ref. [213], i.e. the effect of the medium causing the reduction of relative elongation becomes stronger in proportion to the alloy strengthening and has the highest magnitude during maximum strengthening.

Over-aging an alloy causes a decrease of embrittlement by liquid metal coating.

Fig. 89 also shows the experimental results of copper-beryllium alloy subjected to cold-hardening and tempering. This treatment promotes greater alloy strengthening during aging however the decrease of relative elongation was lower. For example, the greatest decrease of elongation after tempering and cold-hardening was about 60% whereas after only tempering it was close to 100%.

Using cold-hardening after heat treatment as shown in references [236, 237] usually does not cause any changes in the degree of liquid metal effect. Thus, cold-hardening of copper-beryllium alloy after tempering and aging at 370° C for 0.5 and 12 hrs, i.e. up to the highest strengthening (see Fig. 89) does not lead to an increase but to a weakening of the influence of the liquid metal medium. An alloy subjected to maximum strengthening during thermal treatment (tempering and aging at 370° C for 1 hr) discloses an increase of effect of the medium with the increase of cold-hardening degree.

Thermomechanical treatment of the material in a number of cases enables one to increase its strength in a liquid metal medium. In references [238, 239] the influence of thermomechanical treatment on the mechanical properties of 40Kh steel was investigated in air and in contact with eutectic Pb-Sn. Cylindrical specimens 10 mm in diameter with a circular notch were tested. The treatment of the material was carried out in the region of the stress concentrator.

The specimen was placed on a special device and heated by passing an electrical current through it up to the austenitic temperature. Subsequently it was cooled to temperature 400-600° C during which the notch was rolled with profiling rollers. The initial depth of the notch applied on the turning lathe was 1 mm, the radius at the top 0.2 mm and the angle 0.8 rad. When rolling the depth of the notch increased to 1.5 mm while the radius remained the same. After rolling the specimen was subjected to hardening in oil with subsequent tempering. In addition to the above thermomechanical treatment the specimen was subjected to torsional stress. The influence of cold-hardening at room temperature on the liquid metal effect on the steel after hardening and normalizing was also determined.

It is evident from the stress-strain curves presented in Fig. 90 that at a temperature of 400 and 500° C the specimens subjected to quenching fractured under the action of liquid metal in the elastic region undergoing repeated reduction in strength. Some increase in strength is achieved by cold-hardening, rolling at room temperature and thermomechanical treatment by means of torsion. Thermomechanical treatment by rolling leads to the greatest increase in strength. Even though when testing in air this treatment yields an abrupt increase in ductility the specimens undergo brittle fracture when tested in a melt. It should be noted that the method of thermomechanical treatment which proved to be effective for 40Kh steel did not give a positive result for 2Kh13 steel when testing in air or in a melt of eutectic Pb-Sn [239].

The degree of influence of the liquid metal in this case is about the same as after hardening and tempering giving the same level of strength and ductility to steel.

The data presented above indicate that the increase in strength as a result of thermal and thermomechanical treatment, as a rule, intensifies the liquid metal effect. The strengthening effect of 40Kh steel in eutectic Pb-Sn after rolling the stress concentrator is associated mainly with the appearance of compressive stresses in the surface layer of the specimen, since the same thermomechanical treatment but subjecting the specimen to torsional stress does not give similar results. The structural factor exerts apparently an influence on the degree of liquid metal effect when testing precipitation hardening alloys. An increase of the influence of the medium on these alloys should be expected since significant stress concentration in the region of finely divided segregations may appear in them. These segregations are serious obstacles in the path of crack propagation.

h. Influence of chemical composition of liquid metal

Comparison of data on the behavior of solid metal in different liquid metals during deformation indicates that the change in strength and ductility does not occur in every medium. Thus, the action of liquid metals is selective. As indicated above, it is determined by the capacity of liquid metal to decrease the surface energy of solid metal, to produce corrosive fracture in the surface layer and to diffuse into solid metal.

In the final analysis the effect depends on the nature and degree of interaction between atoms of solid and liquid metals.

An attempt has been made in references [199, 240] to find a relationship between the effect of adsorptive decrease in strength and ductility as well as the type of binary phase diagram of the solid-liquid metal systems. It was noted that an abrupt decrease in strength occurs usually when the phase diagram belongs to the simple eutectic type, there is a narrow region of solubility of liquid metal in the solid at the melting point of eutectic and the intermetallic compounds are absent. There will be no change in the mechanical properties if the liquid metal forms a wide region of solid solutions in the solid metal or if they interact with the formation of intermetallic compounds. The liquid metal also does not affect the deformable solid metal when it does not dissolve into the solid metal and they are not miscible in a liquid state.

This rule as indicated by the authors themselves ascertains the most probable trend. However there are exceptions to this rule. For example, M. N. Gavze has established an abrupt decrease in strength of certain pearlite steels in liquid mercury during constant rate tensile test at room temperature [241]. It is well known that mercury is insoluble in iron and consequently should not cause an adsorptive decrease in strength in steel in accordance with this. Corrosive effect in these experiments did not appear due to the negligible solubility of iron in mercury at room temperature [119].

The diffusion factor did not affect since mercury is insoluble in iron and the test temperature was too low for the occurrence of diffusion processes with appreciable rate. Thus, the influence of mercury in these experiments has apparently adsorptive nature.

One of the reasons for the deviation from the above rule is a different electron structure of metal along the grain boundaries than the one inside them as indicated by E. D. Shchukin, B. D. Summ and Yu. V. Goryunov [446] .

Certain metal additions to the liquid metal medium cause substantial change in the magnitude of the effect. Fig. 91 shows the results of tensile tests for zinc single crystals with lead-tin surface coating [192, 242] . Liquid lead is an inactive medium with respect to zinc and does not decrease its strength and ductility. However, lead addition to tin even in a small amount had a detrimental effect on the mechanical properties of zinc. It is evident from Fig. 91 that the true tensile strength and relative elongation of zinc during fracture decrease steadily with the increase of tin concentration in lead to 20%. At a higher concentration the effect of liquid metal remains practically the same.

Table 43 shows the results of tensile tests carried out at a constant rate for 2024-T3 aluminum alloy wetted with mercury amalgam [8] . It follows from the data in the Table that not all of the additions to mercury affect its embrittlement capability.

Thus, sodium, magnesium and cadmium do not change the strength of the alloy in mercury, and the addition of tin seems to somewhat weaken the effect of mercury. However, zinc and gallium even in very small amounts substantially increase the effect of mercury. An amalgam with 2, 4 and 8% Zn exerts practically the same influence probably because the solubility point of zinc in mercury changed and the amalgam consists of two phases, liquid and solid. The same thing occurs for amalgam with 2, 4% and 8% gallium however these compositions represent mixtures of two liquids, one mercury-rich and the other gallium-rich.

The above described influence of additions to liquid metal on the fracture of a high melting metal occurred as a result of a previous introduction of admixtures to the medium. If the metallic elements capable of exerting an adsorptive influence enter into the composition of solid alloy, then they may transfer into the liquid metal as a result of dissolution. Being surface active agents they are adsorbed along the solid-liquid metal interface and cause a decrease in its surface tension. This causes the adsorptive effects to become more intense.

1. Influence of radiation

The radiation of metal by electrons, γ -quanta, protons or neutrons affects its capacity to deform in the liquid metal medium. Under specific conditions the radiation significantly intensifies the liquid metal effect [243-248] .

Fig. 92a shows the curves of uniaxial tension at a constant rate of 10%/min for zinc single crystals coated with mercury. After amalgamation the specimens were exposed to electron radiation in a special apparatus containing a radioactive sample with total radioactivity of 100 Mc. The specimen was 1 mm in diameter and the mercury coating was 5 microns. After irradiating the specimens at a temperature of 25° C tensile tests also under irradiation condition were carried out. Moreover the control soakings of the amalgamated specimens were conducted and subsequently tested without irradiation. It is evident from Fig. 92a that the specimens exposed to radiation for 7 days with subsequent tension under β -radiation almost lose their strength. Their fracture occurs at a stress of about 20 g/mm² with significant deformation. The relative elongation was 1-1.5%. The test specimens also undergo brittle fracture at the basal plane but at a stress greater by a factor of 10. Brief pre-irradiation (for a period of 15 min) causes strengthening on the initial portion of the deformation curve which is associated with a more intensive volume diffusion of mercury in zinc under the irradiation conditions

Fig. 92b shows the change in strength of the amalgamated and non-amalgamated zinc single crystals as a function of the duration of pre-irradiation by electrons. The difference of the irradiation effect on the strength of pure specimens and specimens coated with liquid metal is clearly evident. If the strength of the pure specimens increases steadily with the increase of exposure then the strength of the

amalgamated specimens increased only for small exposures and subsequently decreased. With an exposure of about two days the strength of pure zinc single crystals is lower than that of the amalgamated ones while with longer exposures the ratio between their strength becomes the opposite. An abrupt initial increase in strength is due apparently to the increase in the rate of volume diffusion of mercury into zinc under irradiation. With longer exposures an adsorptive effect of mercury becomes controlling, which apparently is precipitated at the internal surfaces in the defective places of the crystalline zinc lattice in the process of its deformation.

Another factor which intensified the effect of mercury on the irradiated material is the formation of structural defects which may be serious obstacles on the path of crack propagation. Not only the phenomenon of intensive decrease in metal strength as a result of irradiation and liquid metal medium is observed when testing zinc but similar effects also occurred, i.e. when testing tin coated with gallium.

When irradiating single crystal specimens with a directed beam of particles an anisotropic effect of irradiation was established. It was found that in those cases when the beam of particles is directed perpendicular to the basal plane of zinc a significant decrease in specimen ductility occurs. However in the case when the beam is parallel to it the ductility increases. As far as strength is concerned, it is lower than the strength of the amalgamated specimens with no irradiation in both cases. However the strength of single crystals which were irradiated by the beam directed perpendicular to

the basal plane is higher than the strength during parallel basal plane of beam direction. The experiment showed that anisotropic irradiation is more pronounced for relatively heavier particles, i.e. this effect is greater for protons than for electrons.

The dependence of irradiation on the orientation of the beam with respect to the crystal lattice is associated with the possibility of the preferred transmission of the momentum of an impinging particle along a dense row of atoms [249-251] . The following condition should be satisfied in these rows: the ratio of the distance between the atoms to their diameter should be less than two. This is well satisfied in the zinc lattice in the directions $[11\bar{2}0]$, $[1\bar{2}10]$ and $[\bar{2}110]$ in the basal plane. The calculations indicate that the mean energy of the displaced zinc atom during electron and proton bombardment with the intensity used in the experiments on amalgamated zinc single crystals was substantially higher than the threshold energy of displacement [248] .

Chapter 2 - LONG-TERM STRENGTH

a. General mechanisms of failure under statically applied stress

The effect of liquid metals on solids is observed not only during short-term mechanical tests but also under the conditions of long-term endurance tests.

Long-term endurance tests of single crystal specimens in a liquid metal medium have been carried out for relatively short test (usually up to several tens of an hour). The time dependence of the mechanical strength (in a single and polycrystalline state) in an inactive medium is well described as shown by S. N. Zhurkov and co-authors [252-254] by the following empirical equation:

$$\tau = \tau_0 e^{\frac{U_0 - \gamma \sigma}{kT}}, \quad (150)$$

where τ is the time to failure; T is the absolute temperature;

σ is the tensile stress; k is the Boltzmann's constant; τ_0 , U_0 and γ are the constants of a given material. The above equation indicates that, at a constant temperature, the time required to fracture of a metal specimen increases according to the exponential law with the decrease of a statically applied stress. The experiments carried out by V. I. Likhtman and co-authors [255, 256] on single crystals have confirmed the validity of equation (150) and the "structure factor" (γ constant) was found to be dependent on the orientation of single crystal with respect to the tensile stresses.

When the single crystal specimens coated with a liquid metal were tested the nature of their change in strength with time was different.

Fig. 93a shows the results of an investigation at temperatures of 20 and 50° C of the long-term strength of zinc monocrystals with an initial orientation of basal plane, $\chi \approx 50^\circ$. It is evident from the graph that if in an air medium the time for failure changes with the change of stress then the specimens coated with mercury rupture almost instantaneously at a stress close to the yield point while a slight decrease in stress leads to an abrupt increase of time required for failure. Similar results were obtained when testing zinc single crystals with a thin film of liquid gallium. In this case there is an abrupt change in the strength of the specimen within an extremely narrow interval of stresses. There is practically no time dependence of the mechanical strength in this range rather it appears as a threshold strength as shown by E. D. Shchukin and Z. M. Zarozina [7] .

The fracture behavior of polycrystalline samples of certain metals is the same as that of single crystals. For example, threshold strength was observed in long-term endurance tests of polycrystalline zinc coated with mercury (see Fig. 93b) and polycrystalline cadmium coated with gallium. It has been established that amalgamated polycrystalline zinc specimens rupture at room temperature instantaneously at a stress of 1 kg/mm^2 whereas under a stress of 0.96 kg/mm^2 they remain stable (extrapolated by data of tests in air the value of time required for failure under this stress is about 10^{11} sec).

It should be noted that threshold stresses are about the same as the values of brittle strength obtained during tensile test at a constant strain rate. For example, in polycrystalline zinc coated with mercury the threshold stress and fracture strength are about 1 kg/mm^2 .

The long-term endurance tests which showed the existence of a threshold strength were usually carried out without testing the specimens at stresses significantly lower than the threshold stress since the time required to failure in this case is extremely long. In those cases when such a possibility was present it was found that the dependences $\tau = f(\sigma)$ in a liquid metal and in air coincide. This result was obtained for example when testing cadmium in gallium [255, 256] and St. 50 in liquid Pb-Sn alloy at a temperature of 400°C [257].

However, this coincidence of graphs of long-term strength in liquid metal and in air may be only temporary since during creep tests of those same materials the influence of the liquid metal medium accelerated the pile-up process of plastic deformation with time (see Chapter 1). In connection with the fact that creep and long-term strength is a common process [258], the increase of creep rate should inevitably lead to the decrease of time to failure. Therefore for sufficiently long tests (hundreds, thousands of hours) and low temperatures the time dependence of the mechanical strength in materials developing the threshold strength and in a liquid metal medium should be similar to the dependence in air however the value of time to failure will be lower than in air.

Thus the decrease in long-term strength of materials under the action of liquid metal medium occurs in the region of relatively small stresses and large values of time to failure.

Numerous investigations of strength of structural materials under statically applied load and high temperature showed [259-261] that for very long test the experimental data agree well with the power relationship between time to failure and the applied stress

$$\tau = A\sigma^{-n}, \quad (151)$$

where A and n are the constants of the materials independent of stress.

Fig. 94 shows the diagrams of long-term strength for different materials tested in a liquid metal medium and in air. Copper type M-1 was tested for long-term strength in liquid bismuth and in air at a temperature of 350° C. The specimens were machined on a lathe made from bars. Tubular specimens were used with an inside diameter of 10 mm, wall thickness of 0.5 mm and gauge length 50 mm. Liquid metal was poured into the internal cavity of the specimen. To avoid air contact during the tests the interior of the specimen was hermetically sealed by soldering a copper plug to the inlet. Test specimens were filled with argon and a plug was also soldered to their inlet. Long-term strength tests were carried out in uniaxial tension on the UIM-5 device. The temperature was maintained constant within the working area of the specimen and the liquid metal bath. Thus, the testing conditions of copper in liquid bismuth were statically isothermal.

As will be shown in Chapter 5 the controlling factor in the effect of liquid bismuth on copper will be adsorption.

It is evident from Fig. 94a that under the action of liquid metal copper experienced significant reduction in long-term strength. For example long-term strength in liquid bismuth for 100 hours is lower than in air by about a factor of five. With the increase of the test base the difference in the long-term strength becomes steadily greater. It is characteristic that the power relationship of long-term strength is valid also under the conditions of liquid metal effect.

Fig. 94b shows the results of long-term strength test of Armco-iron in liquid zinc at a temperature of 500° C. Machined tubular specimens were used as in the case of copper testing. After preparation the specimens were subjected to annealing in a vacuum furnace (pressure of about 10^{-4} mm Hg) at a temperature of 600° for two hours. The liquid metal was in the internal cavity of the specimen, which was hermetically sealed by welding a steel plug to the inlet. Zinc at a temperature of 500° C diffuses into iron very rapidly [118]. The diffusion factor (see Chapter 5) bears the main responsibility for the reduction of long-term strength of Armco-iron in zinc. At the same time the decrease in long-term strength is also associated with the action of corrosion and adsorption factors.

It follows from Fig. 94b that both in liquid zinc and in air the long-term strength of Armco-iron is characterized by a decrease in stress with an increase of time to failure.

However, the level of long-term strength is significantly lower in liquid metal than in air. Long-term strength of Armco-iron in liquid zinc for 100 hrs is 4.1 kg/mm² and in air 9.8 kg/mm². The difference however in the time to failure under constant stress is much greater. In this case the extrapolated values were compared since tests in liquid metal and in air were carried out because of large difference in long-term strength in these media under various stresses.

Fig. 94c shows the diagram of long-term strength of EI612 (Kh15N35V3T) steel in liquid lithium and in air at a temperature of 1000° C. The steel was studied after heat treatment consisting of quenching in water from 1180° C and aging at 780° C for 10 hrs and 730° C for 25 hrs. The specimens were machined on a lathe and had the same dimensions as specimens of the first two materials. A 400 mm long tube of Kh18N10T steel with the same inside dimensions as the specimen (Fig. 95) was welded to the upper portion of the specimens. The cavity of this elongated specimen was filled with the liquid lithium by a special filtration apparatus at a temperature close to the melting point of lithium. After filling the specimen a thermocouple pocket was placed into the tube and welded to it. The free space in the tube above the lithium surface was filled with argon. Thus, the possibility of a chemical change in liquid metal composition due to interaction with air was eliminated. During long-term strength test the working surfaces of the specimen and the liquid metal were maintained at a constant temperature.

The temperature of the tube with liquid metal was lower than the temperature of the working surface of the specimen and a continuous decrease in temperature occurred in the direction from the specimen to the upper portion of the tube. This caused a convection flow of liquid metal in the internal cavity of the specimen during long-term strength test and the material in the working surface was subjected to continuous dissolution due to the thermal mass transfer process in the conditions described (see Chapter 2). The test was carried out on devices manufactured by the Krasnodar Machine Shop for which special hollow upper grips allowing an elongation tube to be placed inside them were prepared (see Fig. 95).

In all experiments a constant temperature difference of 500° C was maintained between the hot and cold zones (working portion of the specimen and upper portion of the tube respectively). The method of long-term strength test in a convection flow of liquid metal is described in Refs. [80, 262] .

In conformance with the above the controlling factor during impact of the solid metal in a convection flow of a liquid metal is corrosion caused by thermal mass transfer. It is evident from Fig. 94c that under these test conditions the reduction in the material strength occurs. EI612 steel experiences a regular reduction in strength with the increase of long-term strength test in liquid lithium.

Thus, in the region of low stresses and long test in liquid metal, as in the inactive medium, the power relationship between the time to failure and applied stress was observed (Fig. 94).

This fact is of a significant practical value since it enables one to carry out the extrapolation for determining the auxiliary properties of materials designated for long-term exploitation. The power law of long-term strength enables one to write the following expression for coefficient of time reduction to failure in liquid metal K which is equal to the ratio of time to failure in the liquid metal medium to time to failure in air under similar stress and constant temperature:

$$K_t = \frac{A_{\text{ж}}}{A} \sigma^{-(n_{\text{ж}} - n)}, \quad (152)$$

where symbols with index «ж» refer to experimental results in liquid metal and symbols without indices refer to the results of testing in air.

Another coefficient equal to the ratio of long-term strength in the liquid metal medium and in air with similar test duration and constant temperature can be used for liquid metal effect. In conformance with power relationship (151) the expression for this coefficient has the following form

$$K_{\sigma D} = \frac{A_{\text{ж}}^{1/n_{\text{ж}}}}{A^{1/n}} \tau^{1/n - 1/n_{\text{ж}}}. \quad (153)$$

Based on equations (152) and (153) the dependence of the first coefficient on stress and of second on time in logarithmic coordinates is expressed by the straight line. This is convenient for comparing the intensity of the effect under long-term strength conditions of different liquid metals on any solid metal or for comparing the resistance of different solid metals to the effect of the same molten metal.

Failure in liquid metal under a statically applied load occurs not only prematurely but also with lower ductility. Table 44 shows the values of relative elongation during failure of copper specimens, Armco-iron and EI612 steel. Fig. 94 shows the diagrams of long-term strength of these specimens. The data in Table 44 indicate that for all three materials the failure in liquid metal occurs at lower relative elongation than in air. For example, copper specimens when tested in air usually pile up several percent of dislocations during failure whereas the failure in liquid bismuth occurs at relative elongation of 0.15-0.28%. It should be noted that the values of relative elongation should be compared to materials tested in air and in liquid metal for the same duration since with the increase of time to failure the ductility usually drops due to the process itself of long-term strength and intensification of the liquid metal effect during long soakings.

A characteristic feature of delayed failure of solid metals in a liquid metal medium is an intercrystalline propagation of cracks. It should be noted that not only the crack which divided the specimen into two parts is propagated at the grain boundaries but also other less developed cracks. Intercrystalline failure of the material in liquid metal medium occurs also in the case when the material in the inactive medium fails only at the grain.

A regular reduction of strength of materials with the increase of test duration in liquid metal which occurs with more intensity than in air was observed by many investigators.

For example, in Ref. [200] the reduction of long-term strength of nickel base alloy type EI437A in liquid bismuth and eutectic Pb-Bi at a temperature of 700° C was described. In Refs. [263, 264] data are given on the premature failure of brass in liquid mercury. Ref. [265] shows the decrease of long-term strength of copper and brass in liquid tin and solders.

Thus, the above described influence of liquid metal on the time dependence of solid metal strength under small stresses and large values of time to failure has a general nature and is observed when testing different solid-liquid metal couples. However, one should not assume that this influence occurs in any liquid metal during test of long duration. For example, there was no influence of liquid sodium on the long term strength of chromium nickel austenitic steels type 18-8 when tested in static isothermal conditions at temperatures of 540-700° C [34, 266, 267]. The long-term strength of St. 50 under the action of Pb-Bi eutectic at a temperature of 400° C and Pb-Sn eutectic at 500° C did not change [221]. Consequently, during long-term strength test and short duration tensile tests, the action of the liquid metal is selective.

Thus, under the action of liquid metals the time dependence of the strength of the solid metals changes firstly in the region of high stresses and small values of time to failure on account of which the threshold strength appears, and secondly in the region of small stresses and small values of time to failure where the nature of

correlation between stress and time to failure will retain its power law as in the inactive medium. However, failure under these stresses occurs for relatively shorter time intervals. The long-term strength, in the usual understanding of this effect, is substantially the second region. Therefore when speaking about the influence of liquid metals on solids under the conditions of long-term strength test we will bear this region in mind.

b. Influence of temperature

The degree of liquid metal effect on solids under the conditions of long-term strength test depends significantly on the temperature

Fig. 96a shows the results of long-term strength test for copper type M-1 in air and in liquid bismuth at different temperatures. Machined tubular specimens with inside diameter of 10 mm, wall thickness of 0.5 mm and 50 mm long were tested. Before filling them with the liquid metal the specimens were subjected to annealing at 600° C for 2 hrs in a vacuum at a pressure of about 10^{-4} mm Hg. Long-term strength tests were carried out under static isothermal conditions by the method stated in Chapter 1.

Usually the relationship between temperature and time to failure under constant stress in an inactive medium is described by the following equation [252-254, 268, 449]

$$\tau = B \cdot e^{\frac{Q}{RT}}, \quad (154)$$

where T is the absolute temperature; Q is the activation energy of the failure process under the conditions of long-term strength; B is the constant of the material which is independent of the temperature.

In order to explain whether relationship (154) is observed during the liquid metal effect on solid metals, copper specimens were tested at all temperatures under a constant stress of 4 kg/mm^2 . It is evident from Fig. 96a that experimental data fall on a straight line in coordinates "logarithm of time to failure - inversion temperature". Consequently, with liquid metal effect being of an adsorptive nature the exponential relationship (154) is observed.

Fig. 96a also shows the relationship of long term strength of copper in air. It is evident that at identical temperatures the time to failure of copper in liquid bismuth is lower than in air. It is also characteristic that the relative difference between the values of time to failure in air and in the liquid metal is increased with the drop in temperature. The different slope of the lines corresponding to the tests in air and in bismuth indicates the

difference of values of activation energy of the failure process in an inactive medium and in the liquid metal. The calculation indicates that the activation energy of copper failure at a stress of 4 kg/mm^2 is $39.8 \text{ kcal/g}\cdot\text{atom}$ in air, and $23.4 \text{ kcal/g}\cdot\text{atom}$ in bismuth. Thus, the adsorptive-active liquid metal causes the decrease of activation energy of failure of a solid metal under the conditions of long-term endurance tests.

Fig. 96b shows the temperature dependences of long-term strength of Armco-iron in liquid zinc and in air. The iron was tested in zinc (in the same manner as copper in bismuth) under static isothermal conditions. The specimens were annealed at a temperature of 600°C for 2 hrs in a vacuum at a pressure of about 10^{-4} mm Hg . The long-term endurance test was carried out at a stress of 7 kg/mm^2 . Time for fracture of Armco-iron in air under that same stress and different temperatures could not be determined experimentally for a sufficiently large range of temperatures and therefore were obtained by calculation with $\lg \sigma - \lg \tau$ dependences for a temperature of 400 and 500°C . A method, stated in reference [269], was used for the calculation in conformance with which an empirical generalization of the long-term strength equation has the following form

$$\tau = \sigma^{\gamma + \frac{\alpha}{RT}} e^{-\varphi + \frac{\beta}{RT}}, \quad (155)$$

where α , β , γ and φ are constants of the material. They are

associated with the constants in equation (151) by the following relationships

$$A = e^{-\varphi + \frac{B}{RT}}, \quad (156)$$

$$n = -\frac{\alpha}{RT} - \gamma. \quad (157)$$

Based on the experimental data on long-term strength of Armco-iron at 400 and 500°C it was found that the generalized equation for this material can be written in the following form

$$\tau = \sigma^{2.35} \cdot 2.72 \cdot 10^4 / RT e^{-82.0 \pm 13.78 \cdot 10^4 / RT}. \quad (158)$$

A temperature dependence of long-term strength of Armco-iron at a stress of 7 kg/mm² was plotted in Fig. 96b in accordance with equation (158). It is evident from the graph that the exponential relationship between time to failure and inversion temperature, which is valid when testing Armco-iron in an inactive medium, was not observed in the case of liquid zinc effect.

Fig. 96b indicates that at a constant stress the difference in values of time for fracture of Armco-iron in air and in zinc increases with the decrease in temperature. This peculiarity of liquid metal effect is associated with the controlling role of the diffusion factor.

Since with the increase of time the depth of the solid metal layer under the diffusive effect of the medium increases relatively more rapidly than with the increase of temperature, then this explains the deviation from the exponential law of the long-term strength and the increase of the liquid metal effect with the decrease in temperature. A more detailed change in the temperature dependence of long-term strength of the metal caused by the influence of diffusion factor was discussed in Chapter 5.

Fig. 97 shows the diagrams of long-term strength of EI827 nickel-base alloy at temperatures of 600, 750, 800 and 900° C in liquid sodium and in air. The tests in sodium were carried out by the same method as for the EI612 steel in lithium (see Chapter 2). The effect of liquid metal in this case was caused by a corrosive process - thermal mass transfer. The results of static isothermal tests carried out in sodium at a temperature of 750° C confirm the absence of an adsorptive and diffusive influence of the medium (see Fig. 97). The corrosive influence of sodium on EI827 alloy appears, as is evident from Fig. 97, at temperatures higher than 600° C. The nature of liquid metal effect is the same for all temperatures; the reduction of long-term strength of alloy occurs in all cases during which the magnitude of relative decrease becomes larger with the increase of time to failure. The influence of liquid sodium on the alloy is greater the higher the temperature. This is evident from Fig. 98 which shows the dependence

of the coefficient of decrease of long-term strength [see equation (153)] on the temperature.

Table 45 shows the values of long-term strength for EI612 alloy in air and in lithium at temperatures of 700 and 1000° C. Tests in a liquid metal were carried out under the conditions of thermal mass transfer. It follows from the Table that the liquid metal causes a decrease in long-term strength of EI612 alloy for both temperatures but at 1000° C its degree of influence is greater.

Although from the comparison of the coefficient of the decrease of long-term strength for EI827 alloy and EI612 steel under various temperatures it is concluded that the corrosive effect of the liquid metal is intensified with the increase in temperature, however, if the tests were carried out under similar stresses and the values of time to failure were compared with various temperatures then the result would have been the opposite. This can be verified by examining the position of the line in Fig. 97.

Thus, the adsorptive, corrosive and diffusive effect of liquid metal on a solid tested for a long-term strength is characterized by a general rule consisting of the increase of effect with the decrease in temperature when comparing the data for specimens tested under a similar stress.

3. Influence of the initial level of long-term strength

The magnitude of liquid metal effect on a solid during both long-term endurance tests and short mechanical tests depends on the initial level of strength of the solid metal. For evaluating the influence of this factor long-term endurance tests were carried out in convection flow of liquid bismuth specimens made from several austenitic chromium nickel steels having different levels of long-term strength in air at this temperature. The test was carried out on steels of following types: Kh16N16T, Kh16N16M3B, Kh16N16M3BS2, Kh20N12S2, Kh14N18V2B, Kh15N35V3T and Kh20N25M3V6B.

All specimens were tested in liquid metal under a stress of 14 kg/mm^2 and at a temperature of 700°C , the drop in temperature according to the height of the column of liquid metal was about 400°C . The time to failure was determined. Subsequently the long-term strength corresponding to the magnitude of time for failure in liquid bismuth at a stress of 14 kg/mm^2 was calculated by the diagram of long-term strength obtained experimentally for each material in air at 700°C . After this the ratio of long-term strength in bismuth (14 kg/mm^2) to the strength in air was given as the degree of influence of the liquid metal medium.

Fig. 99 shows the dependence of the indicated ratio on the long-term strength of material in air. It is evident from the Fig. that the effect of liquid bismuth on the material increases with the increase of its initial strength. Thus, under the action of thermal mass transfer the

degree of decrease in long-term strength of the solid metal is greater the higher its long-term strength in the inactive medium.

d. Influence of the scale factor

The influence of scale factor on the liquid metal effect was investigated by testing the long-term strength of tubular specimens with different wall thicknesses. The test was carried out for a EI869 nickel alloy at a temperature of 750° C. All specimens were made of this alloy with an internal diameter of 10 mm and a wall thickness of 0.12; 0.25; 0.5; 0.75; 1.0; 1.5; and 2.0 mm. The tests were carried out in liquid sodium under the conditions of thermal mass transfer caused by the drop of temperature in the specimen (see Fig. 95) from 750° C in the working portion to the upper portion of the liquid metal column. Since the scale factor during long-term endurance test of material in the inactive medium also appears as the dependence of time to failure on the cross-sectional dimension of the specimen [270], similar specimens were tested also in air. The internal cavity of these specimens was filled with argon prior to testing and hermetically sealed by welding a plug to the inlet.

The test in liquid metal and in air was carried out under the same tensile stress of 30 kg/mm². The values of time to failure obtained in these experiments are presented in Fig. 100a as a function of the wall thickness of the specimen. It is evident that the lifetime of the specimens decreases with the decreases of its wall thickness.

This conformity applies to tests in sodium and in air. However, in liquid metal the time for failure within the examined range of change in wall thickness, with the exception of extreme values, is lower than in air.

Fig. 100b shows the ratio of time to failure of the specimens in sodium to time to failure in air as a function of the wall thickness. It is evident that this ratio has a minimum value with wall thickness of 0.5 mm and increases with larger and smaller thicknesses. Thus, the influence of liquid sodium due to thermal mass transfer process is exerted on the long-term strength of EI869 alloy only within a limited range of change of the specimen's wall thickness: from 0.15 to 2.0-2.5 mm. It should be noted that the degree of influence of liquid sodium is extremely high. Thus, the maximum value of the effect is 86% at a wall thickness of 0.5 mm and is within the 40-86% range during its change from 0.25 to 1.6 mm.

In addition to the influence on time required for failure the scale factor also affects the relative elongation of the specimen during fracture. Table 46 includes the corresponding values of elongations of specimens for various wall thicknesses tested in sodium and in air. Although all the specimens had a working area 100 mm long, their elongations are comparable since they correspond to uniform deformation of the specimen. This is self-evident from examining the absolute values of elongations which are sufficiently low and only in one specimen exceed 4%.

Data in Table 46 shows that despite the usual scatter of values for this curve, the relative elongation as well as time for failure decreases with the decrease of the wall thickness of the tubular specimen. For all wall thicknesses within the range of 0.25-2 mm the relative elongation of the alloy in liquid sodium is lower than in air and thus the region where the effect of liquid metal environment appears, which is determined by this curve, coincides with the region for the effect determined by the value of time required for failure.

e. Influence of grain size

The influence of the grain size on the long-term strength of the material can be considered in conjunction with the effect of scale factor, since it has been indicated in Ref. [270] that the scale effect is determined by the ratio of average grain diameter to the linear cross-sectional dimension of the working area of the specimen. Consequently, the change in grain diameter with constant specimen dimension leads to the change of the indicated ratio, and this in turn, affects the long-term strength of the material.

Fig. 101 shows the diagram of the long-term strength of LS59-1 brass in liquid mercury and in air at room temperature [255]. Microspecimens with a cylindrical working area of 1 mm in diameter and 5 mm long were investigated. After the preparation the specimens were annealed in order to remove cold-hardening. The annealing was carried out in a vacuum furnace for 2 hrs at a temperature of 300° C.

The specimens with the following three average grain diameters were tested: 50, 220 and 280 μ m. The surface of the specimens was coated with mercury by immersing them into a saturated solution of mercury nitrate. It is evident from Fig. 101 that the long-term strength of brass decreases with the increase of grain diameter in air and in mercury. Consequently, the conformity that a change in long-term strength occurs with the change of the ratio of grain diameter to the cross-sectional dimension of the specimen noted in Ref. [270] was also observed in these experiments. It is also evident from the Fig. that for all values of grain size the long-term strength of brass in mercury is lower than in air. With the increase of grain diameter the effect of mercury increases. Thus, the ratio of long-term strength in mercury and in air on the basis of 5×10^6 sec is 52% at a grain diameter of 50 μ m, 50% at a diameter of 220 μ m and 49% at a diameter of 280 μ m.

A limited range of grain diameter values was used in Ref. [225] and based on the data obtained general conclusions cannot be made. In authors' opinion it is possible that also under those experimental conditions when the controlling factor was the diffusion action, for a sufficiently large range of grain diameters, the conformity similar to the one presented in Fig 100 appeared.

f. The influence of chemical composition of liquid metal

The degree of liquid metal effect on the solid during long-term endurance test depends on the chemical composition of the liquid metal. The presence of other metal components in it may intensify or weaken the effect. These changes may be associated with the change in the interphase surface energy of solid-liquid metal interface. For example, an addition of bismuth into liquid lead causes a decrease in the free energy of its boundary with solid copper. Consequently, during the long-term endurance tests of copper in lead alloys with bismuth the time for failure increases steadily under constant stress when changing the composition of alloys from the predominant bismuth-content to the predominant lead-content (see Fig. 137a).

The influence on the long-term strength of the solid metal in liquid is also exerted by the non-metallic admixtures in the latter. One of the admixtures, intensifying the corrosion action of certain liquid metals, is oxygen. Fig. 102 shows the diagram of the long-term strength of EI765 nickel-base alloy in air and in sodium with pure and highly contaminated oxygen. It is evident from the Fig. that the alloy has the same long-term strength in air and in pure sodium. The contamination of liquid metal by oxygen causes an abrupt decrease in long-term strength of the alloy. Thus, for example, the long-term strength of EI765 alloy exposed for 100 hrs in air and in pure sodium is 20 kg/mm^2 , and in contaminated sodium it is only 8 kg/mm^2 .

The decrease in long-term strength due to oxygen-content in sodium was also established when testing EI869 nickel alloy at a temperature of 750°, EI851 steel at 700° and Kh2M steel at 593° C [271] (see also Chapter 5). In contrast to these experiments, S. T. Kishkin and G. P. Benediktova observed an increase in long-term strength of EI437A and EI617 alloys at a temperature of 1000° C and 1Kh18N9T steel at 900° C in an unpurified liquid sodium with carbon when compared to long-term strength in air [272-274]. Fig. 103a shows the experimental results for EI617 alloy. It is evident that for all the values of stress, the time for failure of the specimen in sodium is higher than in air. Consequently, the long-term strength of the alloy after 100 hrs in an unpurified sodium exceeds the corresponding strength in air by a factor of two.

The tests of EI617 alloy in pure sodium indicated that the time dependence of strength coincides in this case with the one obtained in air. Metallographic analysis of fractured specimens revealed the presence of a diffusion zone, the hardness of which is higher than the hardness of the starting material, at their surfaces on the side of the unpurified sodium. X-ray analysis of precipitations, electrolytically isolated from the surface layers of EI617 alloy, which is in contact with sodium for 25 hrs has been carried out. It has been established that Me_{23}C_6 carbides and titanium nitride were formed in the surface layer. The presence of these phases in alloy leads to its strengthening and to the decrease of the plastic deformation capability (decrease of creep rate).

After identical time intervals, the specimen tested in contaminated sodium has a lower relative elongation than the specimen tested in air with the same initial stress. This difference in relative elongation remains for the entire test up to the fracture of the specimen. Fig. 103b shows a significant decrease in relative elongation during fracture of the specimens in an unpurified sodium. Thus, if the specimens of EI617 alloy in air are fractured at an elongation from 40 to almost 80%, then in sodium they fracture at 15-20%. As a result of a significant creep rate of the specimens in air, followed by necking-down, their long-term endurance test* occurs at an abrupt increase of true stress with time. According to calculations presented in Ref. [272], during fracture the true stress in specimens of EI617 alloy exceeds the initial by more than a factor of two. In contrast to the specimens tested in air in contact with unpurified sodium, they are deformed less and consequently the increase in true stress is smaller. This increase at the end of testing (100 hrs) is only 25% of the initial stress.

Thus, the presence of carbon and apparently nitrogen in sodium leads to the formation of a diffusion layer on the surface of the material causing the increase in long-term strength due to a less intensive increase of true stresses with time.

*The test was carried out under constant load.

The indicated admixtures in sodium were formed from organic substances (kerosene, oil, etc.) in which sodium was stored and from which it was not purified [272-274]. According to the opinion of the authors, the increase in strength of the materials in an unpurified sodium during brief tests [272, 273] will not occur in tests of long-duration, if the material abruptly loses the ductility. The strengthening of nickel alloy does not occur with a test duration of about 500 hrs [274].

g. Influence of chemical composition of the solid metal

The effect of liquid metal on a solid metal during long-term endurance test depends substantially not only on the chemical composition of liquid metal but also on the composition of the solid metal. In many cases a noticeable increase or weakening of the effect in comparison with the influence on pure metal might be expected even at relatively low content of a secondary component in alloy. This influence of alloy may be observed, for example, in the decisive role of the corrosion process, which occurs at the grain boundaries, if the presence of the secondary component substantially changed the rate of this process. In the case of the mixed diffusion-adsorption action a small content of alloy component may exert a significant influence on the effect, if this component is sorophilic and the liquid metal diffuses mainly at the grain boundaries with diffusion rate as function of alloy content.

The adsorption action of liquid metal may originate or be intensified in the case of a small amount of any alloying element which penetrates into a liquid metal solution due to the dissolution of basic alloy components and after being adsorbed at the surface of the solid alloy is capable of significantly changing the magnitude of the surface interphase energy of the solid-liquid metal interface. From the processes indicated the latter apparently played the decisive role in decreasing the long-term strength of EI437B alloy at a temperature of 800° C in liquid sodium under static isothermal conditions [275] since other nickel-base alloys (EI869, EI765, EI827) with the same oxygen content in sodium and at similar temperature (750° C) did not decrease the long-term strength [276].

It is quite natural that the influence on long-term strength of a solid metal in a liquid metal medium is exerted not only by small alloying additions but also by large additions. In this case their influence mechanisms may be different. For example, selective corrosion can play a significant role in breaking the stressed material. Fig. 104 shows the dependence of ratio of long-term strength of brass in liquid tin and in air on the zinc-content at a temperature of 240° C plotted according to data in Ref. [265]. It is evident that this ratio characterizing the degree of interaction of liquid metal practically does not change with the increase of zinc concentration in brass up to 18%. Further increase of its content intensifies the influence of tin on brass.

Thus, if the influence coefficient of tin on pure copper is 0.56 while on brass containing 18% zinc is about 0.51 then on brass with 38% it is only 0.21. This influence of the secondary component indicates the decisive role of the corrosion factor in the influence of tin on brass, since the solubility of zinc in liquid tin at 240° C is about 10% by wt., and the solubility of copper in tin is less than 1% by wt. [119].

Chapter 3 - CREEP

a. General principles of creep of solid metals in a liquid metal environment

In many instances a liquid metal medium exerts an influence on the creep process of solid metals under constant stress. This influence involves the easing of the deformation process and increase of the creep rate in the liquid metal as compared with the inactive medium for identical stress in both experiments. It has been established that solid metal experience the action of a liquid metal medium under creep conditions, being both in a single- and polycrystalline state.

Creep tests of single crystals in a liquid metal were first carried out by V. I. Likhtman, V. A. Labzin, N. V. Pertsov and Yu. V. Goryunov [277-279]. Specimens with cylindrical working area of 0.5-1 mm in diameter and 10-15 mm long were tested in uniaxial stress. Liquid metal was deposited at the surface of the specimens electrolytically or chemically. The thickness of the coating was usually 5 microns.

Fig. 105 shows the characteristic creep curves for pure zinc single crystals and coated with liquid tin at a temperature of 350°C and stress 19.1 g/mm^2 . It is evident from the Fig. that under the action of the liquid metal the plastic deformation of zinc occurs at a significantly greater rate.

The examination of relative positions of curves enables one to conclude that the creep rate of zinc single crystals in liquid tin is greater than in air both at the first stage (damping creep) and in the second stage (steady-state creep). Measurements of initial creep rate of zinc indicated that this characteristic curve of the process is also greater when testing single crystals in liquid metal than in air [278]. When increasing the stress the initial creep rate of zinc single crystals in tin increases in the same manner as when testing in air but always has greater magnitude.

It should be noted that the influence of liquid metal coating on creep of single crystals is observed at a temperature both lower and higher than the threshold temperature of induced brittleness (upper temperature boundary of embrittlement according to the definition given in Chapter 1).

Creep tests of zinc single crystals in mercury, which were carried out at room temperature, gave a more complex picture of liquid metal action than the one established in experiments on zinc coated with tin.

In this case it was found that for high stresses, close to the yield point, the single crystals under the action of mercury are strengthened, i.e. are deformed with lower rate than under that same stress in air. For stresses of lower magnitude, for example 0.7 of yield point, the mercury as well as tin eases the plastic deformation of zinc. This unusual action of mercury is associated with the influence of its volume diffusion in zinc [240]. For higher stresses and subsequently more intensive plastic deformation the diffusion occurs at a greater rate. This in turn leads to a blocking of sources generating dislocations to a greater extent than for low stresses.

The strengthening of zinc due to volume diffusion of mercury was confirmed by the tensile tests carried out for single crystals at the liquid nitrogen temperature after keeping them in contact with mercury at room temperature. It was found that normal and shear stresses during fracture of single crystals steadily increase with the increasing duration of diffusion.

Strengthening due to alloying under creep conditions was also observed when testing cadmium and tin single crystals in liquid mercury [279]. However, the action is not characteristic of a diffusion factor in these experiments. In all probability, it is specific for testing solid-liquid metal couple, which do not differ greatly in their melting point values. If the melting point of the metal coating is considerably lower than the melting point of the deformed metal, then both the diffusion and adsorption action eases the plastic deformation process under constant stress.

The experiments carried out for polycrystalline metals indicated that they are similar to single crystals, i.e. disclosed an increase in creep rate under the action of a liquid metal medium. The influence of molten metal in this case is also observed in the first and second stages of the process. The relative position of creep-time curves in polycrystalline specimens, which were tested in contact with liquid metal and in air, is the same as indicated for zinc single crystals in Fig. 105. Usually within a wide range of stresses and creep rates the dependence between them is well described [259, 260] by the power law

$$\dot{\nu} = c\sigma^m, \quad (159)$$

where $\dot{\nu}$ is the steady-state creep; c and m are constants of the material independent of stress.

Creep tests in a liquid metal medium indicated that equation (159) is also observed in this case. The dependence of steady-state creep on the stress for copper of type M-1, which was tested at a temperature of 350° C in air and in liquid bismuth, is shown in Fig. 106b as an example. The experiments were carried out on machined tubular specimens with a working area of 10 mm in inside diameter, wall thickness of 0.5 mm and 50 mm long. The test conditions in the liquid metal were static isothermal and corresponded to those described in Chapter 2. Prior to creep testing the specimens were subjected to annealing in vacuum (about 10^{-4} mm Hg) at a temperature of 600° C for 2 hrs.

It is evident from Fig. 106b that in logarithmic coordinates the dependence of steady-state creep of copper in liquid bismuth as well as in air is described by the straight line, i.e. it corresponds to equation (158). However, the line corresponding to tests in liquid bismuth is located on this graph below the line corresponding to the tests in air. This indicated that under identical stresses the steady-state creep of copper in bismuth is greater than in air. It also follows from Fig. 106b that with the decrease of stress the relative difference of creep in liquid metal and in air increases.

In view of the fact that equation (159) is valid both during creep tests of solid metal in liquid and in air, the degree of influence of liquid metal can be easily characterized by the magnitude of ratio of creep in liquid metal to the creep in air under identical stresses. The experimentally obtained ratio can be called the coefficient of influence of liquid metal or coefficient of increase of steady-state creep in liquid metal. Its expression has the following form

$$K_{\text{ж}} = \frac{\epsilon_{\text{ж}}}{\epsilon} \sigma_{\text{ж}}^{m-m}, \quad (160)$$

where symbols with indices «ж» refer to tests in liquid metal, the symbols without indices refer to tests in air.

For the influence characteristic of liquid metal on the steady-state creep of solid metal another coefficient can be used. This is equal to the ratio of creep limits in the liquid metal and in air corresponding to the identical value of creep rate.

It is convenient to use this coefficient in evaluating the influence of temperature when there are several isotherms similar to those presented in Fig. 106. The coefficient of decrease in creep limit of solid metal in liquid in conformance with equation (159) has a power dependence on creep

$$K_{\sigma_{\text{н}}} = \frac{\sigma^{1/m}}{\sigma_{\text{ж}}^{1/m}} \nu^{1/m_{\text{ж}} - 1/m}. \quad (161)$$

As a result of increase of creep rate in a liquid metal medium the value of the first coefficient is greater than unity while the value of the second coefficient is lower. If the liquid metal does not affect the creep rate of the solid metal then both coefficients are equal to unity.

Under the action of a liquid metal elastic strain of solid metal occurs at a greater rate not only for steady-state creep but also for damping creep as was indicated earlier. Data on the influence of the liquid metal on the creep process in the first stage can be obtained by comparing the values of mean creep rates in this stage in specimens tested in a liquid metal medium and in air. Let us calculate the mean rate ν_1 as the ratio of the elongation δ_1 , accumulated by the specimen for the first stage, to the duration of the stage τ_1 , i.e. $\nu_1 = \delta_1 / \tau_1$. Fig. 106a shows the mean creep rate for the first stage as a function of stress for annealed copper of type M-1 at a temperature of 350° C. It was found that the power relationship is well fulfilled between these values.

It is evident that the lines, which were plotted according to experimental results of copper in liquid metal and in air, divide. The value of mean creep rate in the first stage as well as that of the steady-state creep rate is greater when testing copper in liquid bismuth than when testing in air and the relative difference between them increases with the decrease of stress.

The effect of the liquid metal on the solid tested for creep leads to the shortening of the duration of all creep stages . Fig. 107 shows the dependences of duration of the first, second and third stages and relative elongation corresponding to these stages on the stresses for copper of type M-1, which was tested in air and in liquid bismuth. It is evident from the graphs that the action of liquid metal affects the duration of the creep stage and the value of the relative elongation in the third stage but does not change the relative elongation in the first and second stages . The effect of liquid bismuth on copper is determined by the adsorption factor. However, the regularities of changes in creep characteristics described above are observed also in the case of controlling action of other factors. Fig. 108 shows the dependence of steady-state creep of 1Kh14N14M3B steel on stress at a temperature of 700° C in air and in the convection flow of sodium. It follows from the graph that under the conditions of action of thermal mass transfer the power dependence of creep on stress holds . The liquid metal, exerting a corrosion action, causes an increase of creep rate during which the effects are greater the lower the stress.

It has been established by the Armco-iron tests in liquid zinc that the action of the diffusion factor on creep rate is similar to the action of adsorption and corrosion factors (see Chapter, Fig. 123).

The influence of liquid metals on the creep process of solid metals is observed not only in the case of uniaxial stress. In Refs. [280, 281] creep tests of single crystalline specimens under the conditions of torsion were described. It has been established that the mechanisms of influence of liquid metal coatings on the creep process of single crystals under constant torsion is the same as under constant tensile stress [277-279].

b. Influence of temperature

The magnitude of the effect of liquid metal on the creep process of solid depends substantially on the temperature. The influence of temperature has been established in the experiments with single- and polycrystals. Table 47 shows the experimental results for creep of pure zinc single crystals and coated with tin under various temperatures.

A stress 0.7-0.8 of the yield point was assigned to the specimens at a suitable temperature. The data in Table 47 indicate that with the increase in temperature the effect of liquid tin increases. The testing of zinc single crystals at 200° C showed the decrease of creep rate due to the action of a solid surface metal film, which hinders the escape of dislocations at the surface of the specimen.

Fig. 109 shows the temperature curves of steady-state creep rate of metals in the polycrystalline state for copper and Armco-iron. Specimens with a wall thickness of 0.5 mm were tested. The testing conditions in liquid metal were static isothermal. The purpose of this test was to verify the application of an exponential dependence of the steady-state creep rate on the inversion temperature experimental results in a liquid metal environment, which was fulfilled in the absence of the influence of the environment [268]:

$$v = v_0 e^{-Q_0/RT}, \quad (162)$$

where T is the absolute temperature;

Q_0 is the activation energy of creep

R is the gas constant;

v_0 is the coefficient independent of temperature.

Equation (162) is applicable to the experimental results for creep under various temperatures but identical stresses. Therefore the creep rate of copper in liquid bismuth was determined under constant stress of 4 kg/mm² while creep rate of Armco-iron in zinc was determined under a stress of 7 kg/mm². Since a stress of 7 kg/mm² is too low for iron when testing within a given temperature range and is practically impossible to determine the creep rate under its action in view of extremely long-term experiments, a method based on the application of the following two empirical equations was developed for calculating creep rate: creep rate as a function of stress (159) and temperature (162).

Assuming that coefficients in equations (159) and (162) are certain functions of the temperature and stress respectively, it is possible to write the identity

$$\ln v_0(\sigma) - \frac{Q_*(\sigma)}{RT} \equiv \ln c(T) + m(T) \ln \sigma. \quad (163)$$

Differentiating it successively with respect to σ and T we obtain the equations

$$-\frac{1}{RT} \cdot \frac{dQ_*(\sigma)}{d\sigma} + \frac{1}{v_0(\sigma)} \cdot \frac{dv_0(\sigma)}{d\sigma} \equiv m(T) \frac{1}{\sigma}, \quad (164)$$

$$\frac{dQ_*(\sigma)}{d\sigma} \cdot \frac{1}{RT^2} \equiv \frac{1}{\sigma} \cdot \frac{dm(T)}{dT}. \quad (165)$$

It follows from equation (165) that

$$Q_*(\sigma) = \alpha_* \ln \sigma + \beta_*, \quad (166)$$

$$m(T) = -\frac{\alpha_*}{RT} - \gamma_*. \quad (167)$$

where α_* , β_* , and γ_* are the constants of the material independent of temperature and stress.

For determining $v_0(\sigma)$ from equations (166), (167) and (164) we obtain a linear differential equation

$$v'_0(\sigma) + \frac{\gamma_*}{\sigma} v_0(\sigma) = 0, \quad (168)$$

the solution of which we find in the form

$$v_0(\sigma) = e^{-\alpha_* - \gamma_* \ln \sigma}. \quad (169)$$

From equations (163), (166), (167) and (169) we obtain

$$\ln c(T) = -\varphi_* - \frac{\beta_*}{RT} \quad (170)$$

or

$$c(T) = e^{-\varphi_* - \beta_*/RT}. \quad (171)$$

Finally a generalized equation, describing the dependence of steady-state creep rate on stress and temperature, is written in the form

$$\dot{\nu} = c^{-\varphi_* - \beta_*/RT} \sigma^{-\gamma_* - \alpha_*/RT}. \quad (172)$$

Using equations (167) and (171) it is possible to find four constants of equation (172) from two experimentally determined isotherms "creep rate-stress" and then plot the creep vs temperature curve for any stress of interest. These calculations were carried out for Armco-iron using in this case the results of tests at temperatures of 400 and 500° C.

It has been established that the generalized equation of creep has the following form

$$\dot{\nu} = e^{-97.6 - \frac{20.58 \cdot 10^4}{RT}} \sigma^{-9.44 + \frac{3.68 \cdot 10^4}{RT}}. \quad (173)$$

Let us not refer to graphs in Fig.109. It is evident that the action of an adsorptive-active liquid metal (bismuth) on copper does not change the functional relationship between the steady state creep and temperature

However, its action leads to a substantial increase of creep and the effect becomes greater the lower the temperature. The easing of plastic deformation in an adsorptive-active melt was also expressed by a decrease of activation energy of creep. Its magnitude for copper, deforming under a stress of 4 kg/mm^2 , is $42.5 \text{ kcal/g. atom}$ in the inactive medium while under the action of liquid bismuth it decreases to $34.5 \text{ kcal/g. atom}$.

The creep vs temperature curve of Armco-iron in liquid zinc (see Fig. 109b) is of different nature. As a result of action of diffusive active liquid metal (see Chapter 5) creep increases also for each selected value of temperature while the exponential dependence (106) is not fulfilled. However in this case, as in the preceding, the influence of the liquid metal at low temperature is relatively stronger than at high temperature.

Fig. 110 shows the experimental results of the influence of temperature on the corrosion action of liquid sodium on EI827 alloy under creep conditions. The testing method was the same as the one described earlier in Chapter 2. The corrosion action of sodium on the material when testing by this method was determined by the thermal mass transfer which was caused by a drop in temperature (about 400°C) vertically of the column of liquid metal in the internal cavity of the specimen. Test specimens were filled with argon and hermetically sealed by welding a plug to the inlet. Tests were carried out in air.

It is evident from Fig. 110 that at a temperature of 600° C liquid sodium does not affect the creep rate of alloy EI827. At higher temperatures the creep rate in sodium is higher than in air under that same stress. With the increase in temperature the effect of molten metal is increased. This is evident by the increased distance between lines $\lg \dot{\nu} - \lg \sigma$ for testing in sodium and in air with the increase in temperature and also by the data in Table 48 in which the values of the coefficients of decrease of creep rate of liquid metal are given. Table 48 also shows the results of creep tests for EI612 steel in air and in a convection flow of lithium, which were carried out by that same method as for alloy EI827.

Data in the Table indicate that the increased temperatures lead to the increase of the influence of sodium and lithium on creep rate of both materials under investigation. However, it should be noted that the corrosion action of liquid metal as well as adsorption and diffusion is characterized by the decrease of the effect with the increase in temperature when comparing the results of creep tests under identical values of stress. This conclusion can be made for example by comparing the relative positioning of the lines in Fig. 110.

c. Influence of scale factor

Since the effect of liquid metal on the creep process of solid is associated with their surface interaction, then it should significantly depend on the cross-sectional dimensions of the specimens (details).

Based on this one may assume the existence of a certain upper limit of cross-sectional dimensions for which the effect disappears. The experiments carried out under the conditions of corrosion action of a metallic melt also showed the existence of a lower limit. Fig. 111a shows the dependence of steady-state creep rate of specimens made of alloy EI869 on the thickness of their walls. The tests were carried out on machined tubular specimens. The inside diameter of the specimens was 10 mm and wall thicknesses 0.15; 0.25; 0.5; 0.75; 1.0; 1.5 and 2.0 mm. All the tests were carried out at a temperature of 750° C, the specimens were loaded in uniaxial tension at a stress of 20 kg/mm². The effect of liquid metal(sodium) on the specimen occurred due to thermal mass transfer caused by a drop in temperatures (about 350° C) in the internal cavity of the specimen vertically along the column of the liquid metal (see Fig. 95).

It is evident from Fig. 111a that the creep rate of the material depends on the wall thickness of the tubular specimen in the inactive medium. The increase of steady-state creep rate with decreasing wall thickness is associated with the metal approaching the single crystalline state and with the increase of the role of the surface factor in the creep process [270]. As evident from the Fig. the creep of specimens with small wall thickness also depends on the corrosion action of liquid sodium. It leads to a greater increase of creep rate for specimens with a wall thickness from 0.15 to 1 mm.

The degree of influence of liquid metal on the creep rate of specimens with different dimensions can be easily determined by the magnitude of the ratio of their creep rates in sodium and in air. The dependence of this ratio on the thickness of the wall is shown in Fig. 111b. It follows from the above that the highest influence is exerted on the specimens with micromillimeter wall. The increase in the creep rate in this case is almost threefold. The change in wall thickness as compared to 0.5 mm leads to smooth decrease of the effect.

d. Influence of chemical composition of liquid metal

The magnitude of the effect easing the plastic deformation of solid metal in liquid under creep conditions as well as under other types of mechanical tests depends also on the composition of liquid metal. In this case both large and small amounts of admixtures can play a significant role. The change of chemical composition of liquid metal sometimes leads to a qualitative change of the effect of liquid metal. Fig. 112 shows the dependence of the ratio of steady-state creep rates in liquid metal and in the inactive medium (argon) on the composition of liquid metal for zinc single crystals tested at a temperature of 350° C [277].

It is evident that in pure lead the creep rate for zinc is even lower than in argon. Small tin addition to the liquid metal cause an increase in the creep rate and the ratio of rates becomes greater than unity.

Further increase of tin concentration in lead is accompanied by a continuous increase of the effect which reaches a maximum magnitude in pure tin. This action of the secondary compound of the liquid metal solution (tin) is associated in the given case with the fact that this metal is surface active with respect to zinc, while lead is not.

A bismuth addition to lead during creep test of polycrystalline copper behaves similarly to a tin addition to lead during creep test of zinc single crystals. In this case the nature of change in steady-state creep and the mean rate in the first stage is similar to the change of magnitude of surface interphase energy, which occurs with the increase of bismuth content in lead (see Fig. 136 and 138).

Certain nonmetallic admixtures also exert an influence on the magnitude of the steady-state creep rate of the solid metal in liquid. Fig. 113 shows the steady-state creep rate of EI851 steel as a function of stress at a temperature of 700° [282]. The tests were carried out in uniaxial tension of tubular specimens with a wall thickness of 0.5 mm. The experiments in the liquid metal (sodium) were isothermal static. Pure sodium containing 0.01 wt. % O_2 was used and sodium inside the specimen containing 1% O_2 was contaminated with an addition of sodium peroxide. It follows from Fig. 113 that pure sodium does not affect the creep rate of EI851 steel, while sodium with oxygen admixture causes it to increase, becoming higher as the stress falls and consequently the absolute value of the initial creep rate.

The influence of oxygen admixture in sodium on the creep process of the metal does not always increase its rate as in the case of EI851 steel. A strong change in the initial creep curves for deformation-time making it impossible to isolate the usual three stages on them was established by testing a nickel-base EI869 and EI765 alloys in sodium, which was highly contaminated with oxygen (10% by wt. of liquid metal in the specimen). These changes arose from the chemical interaction between alloys and the sodium oxide. When examining sections under the microscope a wide range of highly etching reagents was observed in the inner surface of the specimens.

The effects of the increase of long-term strength of EI437A and EI617 alloys at a temperature of 1000° C and 1Kh18N9T steel at 900° C in an unpurified sodium was described in Chapter 2. This is due to diffusion into alloys and carbon steel and apparently due to nitrogen in sodium. The surface layer formed as a result of the diffusion processes has a lower capacity of plastic deformation. The creep rate of specimens during testing in an unpurified sodium was lower than the creep rate in air and in the pure liquid metal. The decrease of the creep rate is thus another of the many effects of admixtures in liquid metal on the deforming solid metal.

Chapter 4 - FATIGUE STRENGTH

a. General principles of failure under cyclic load

A liquid metal medium exerts an influence on the strength of solid metals when testing them not only under constant but also under variable load. The decrease in fatigue strength of the material is usually due to this influence.

Most of the fatigue tests in the liquid metal medium were carried out under cyclic bending. It has been established in many cases that the effect of liquid metal becomes progressively stronger with the increase of testing base. This effect was observed for example during fatigue test of alloy EI617 in molten lead at a temperature of 700° C (Fig. 114). These experiments were carried out on the Shenka machine for specimens with a cylindrical working area of 7.5 mm in diameter [283]. During the test the specimen was in a liquid metal bath.

It is evident from Fig. 114 that with the increase of the number of cycles for failure and respectively with the decrease of stress amplitude the discrepancy in the fatigue curves for alloy EI617, corresponding to the results of testing in air and in lead, is increased. In this case the material does not have a true endurance limit in air and in liquid metal. The absence of an endurance limit when testing in air is due to the effect of high temperature: irreversible changes occur in the specimen at small stress amplitude leading to failure after a finite number of cycles.

The disappearance of a true endurance limit with an increasing test temperature has been established in many materials [284-288].

In addition to alloy EI617 a similar effect of liquid metal on the fatigue strength was determined when testing alloy EI437 in lead, bismuth and their eutectic at a temperature of 700° C [283].

In some papers a different dependence of the degree of influence of liquid metal on the endurance of the material upon the number of cycles was observed than the one indicated in the above experiments. Individual materials experience a greater effect of molten metal the higher the stress amplitude. The intensification of the aggressive effect of the liquid metal medium with increasing stress amplitude was observed during cyclic bending tests of 70/30 brass coated with mercury at room temperature (Fig. 115) [289]. In this case the material has a true endurance limit in air and in the liquid metal. The decrease in a true endurance limit of brass occurred under the action of liquid mercury. The effect of mercury in the region limited endurance was exerted to an even greater degree.

The intensification of the liquid metal effect with increasing stress amplitude similar to that experienced by 70/30 brass in mercury occurs apparently in those cases when the controlling factor is the initial strength of the material. The empirical equation determined for material fatigue in the inactive medium within the range of limited endurance has the form

$$N = Q e^{-q \Delta \sigma}, \quad (174)$$

where N is the number of cycles for failure; $\Delta \sigma$ is the stress amplitude; Q and q are the material constants. At high temperature and low frequency of changes in load, when there is no endurance limit, another equation is valid [184, 185]

$$N = Q_0 \Delta \sigma^{-q_0}, \quad (175)$$

where Q_0 and q_0 are the material constants.

During fatigue tests of the material in the liquid metal medium, equations (174) and (175) are also valid but their coefficients are different.

The degree of influence of the liquid metal medium on the fatigue strength of a solid can be characterized by the ratio of the endurance limits (arbitrary and true) in liquid metal and in an inactive medium with an identical testing base

$$K_W = \frac{\sigma_{1W} (\text{ж. м.})}{\sigma_{1W} (\text{в. в. в.})}. \quad (176)$$

This ratio will be called the coefficient of liquid metal effect on the fatigue strength of the material. It is evident that in the case of strength decrease under the action of molten metal the coefficient takes on the values within the range of 1 to 0, with the increase of endurance (see Chapter 4) they become greater than 1.

The fatigue strength of a solid metal is decreased under the action of a liquid not only in the case of symmetrical bending test, as in the examples indicated above, but also under other types of loading. Thus, the effect of tin on soft steel was observed when testing in a symmetrical tension-compression cycle at a temperature of 300° C [289]. The decrease in true endurance limit due to the tin influence and also in resistance to cyclic load within the range of limited endurance was observed.

The decrease of fatigue strength of the material in the liquid metal medium was established only when loading under tensile stresses, which varies with time according to a rectangular cycle [283]. The specimen was under load for 25 min and 5 min without load. The test temperature was 700° C. Although the frequency of cycles was rather low the fracture was of a fatigue nature since the time prior to fracture in this case was significantly less than under constant load, i.e. when testing for long-term strength. The experiments have indicated that alloys EI437A and EI617 undergo a decrease in plastic strength in lead and eutectic Pb-Bi under this type of load. A comparison with the result of the test of alloy for long-term strength at that same temperature and in those same media indicates that even for a large magnitude of half-period during tensile stress, the influence of the liquid metal medium under a cyclic load is relatively lower than under a constant load.

A continuous increase of the effect of liquid metal with the increase of number of cycles to failure has been determined by the fatigue test of alloys EI437A and EI617 under tensile stresses [283]. Fatigue tests with this type of loading of 7075-T6 aluminum alloy specimens in mercury at room temperature showed an opposite mechanism [8].

The decrease in cyclic strength of materials as a result of molten metal effect was observed in loading of the specimens under torsion. Fig. 116 shows the results of fatigue tests under this type of loading of specimens made of 70/30 brass with an uncoated surface and coated with liquid mercury [290]. The specimens were in a cylindrical rod form 3.56 mm in diameter and 44.5 mm long. Under the action of the applied torque the specimens first were twisted for a determined angle into one direction and subsequently into the opposite direction. Thus, the test was carried out by the method of a specified amplitude of deformation. The peculiar feature of the test was the application of deformation on the specimens which exceeded the elastic deformations, i.e. the specimens were tested for fatigue in the elastic-plastic region. Under these conditions the tendency towards strengthening of the material was clearly defined (the increase of torque with the amplitude value of deformation) as the number of cycles increases. In this connection the experimental results can be given in terms of torque as a function of the total angle of twist. The total angle of twist is proportional twice the amplitude of deformation (given in degrees) for a number of cycles; consequently in this case all the stresses irrespective of sign are summarized.

As is evident from Fig. 116, in the indicated test conditions the strengthening of brass with the increase of the total angle of twist occurs with identical intensity with and without the effect of mercury on the specimens. The strengthening becomes greater the higher the amplitude of deformation. The influence of liquid metal results in the decrease of the total angle of twist during failure as compared to the specimens without the coating. This effect increased with the increase of the deformation amplitude. Thus, fatigue tests of 70/30 brass under torsion in the elastic-plastic region showed a strengthening of the effect of liquid mercury with an increasing amplitude of deformation.

The decrease in fatigue strength of St. 40 under the action of mercury at room temperature has been determined in Ref. [291] when loading the specimens in the elastic-plastic region. The wire specimens were bend tested in a special device [292]. Clamps with different jaw radii were used. It is evident that with the decrease in their radius the amplitude of plastic deformation of the specimens increases. In accordance with this the number of bends endured by the specimens without failure should decrease.

As is evident from Table 49, in which the experimental results are given, this conformity was observed when testing the specimens with and without mercury coating. The action of mercury on steel results in the decrease in the number of bends in the wire specimens tested for failure as compared with an uncoated specimen with an identical jaw radius in both cases.

The evaluation of the liquid metal effect by the magnitude of the ratio of number of bends prior to failure both in liquid and in air indicates (see Table 49) that with the decrease of jaw radius the effect increases. This suggests that the influence of the medium becomes greater the higher the amplitude of plastic deformation. Thus, the results in Refs. [290] and [291] are in agreement.

Microstructural investigation of specimens fractured during fatigue tests showed that under the action of the liquid metal medium the materials develop a tendency towards an intercrystalline fracture. Cases were noted when under those same conditions the material in air is fractured along the grain and in the liquid metal along the grain boundaries [283]. Sometimes a transition from fatigue to intergranular cracking occurs in the material under the action of liquid metal although there is no decrease in endurance. This effect was observed during fatigue test with a symmetrical tension-compression cycle of chromium-nickel 18-8 steel in liquid sodium at a temperature of 300° C [289].

Similar observations were also made by the present author during the cyclic bend test with symmetrical loading of several heat-resisting steels in liquid sodium (Table 50). These experiments were carried out on the so-called Oding's ring specimens at assigned amplitude of deformation by the method described in Refs. [185, 293].

It should be noted that together with the tendency towards intergranular cracking of materials in liquid metals in certain cases the failure occurs along the grain, although there is no decrease in fatigue strength.

b. Influence of cold-hardening

There are no systematic investigations of the influence of preliminary plastic deformation of the material on its fatigue strength in a liquid metal medium. However certain conclusions on the effect of this factor can be made based on Refs. [289, 291, 294].

Fig. 117 shows the diagram of fatigue strength under symmetrical bending of 70/30 brass in air and in liquid mercury [289]. Tests were carried out on wire specimens (2.54 mm in diameter) which endured significant plastic deformation in the process of cold-drawing.

It is evident from Fig. 117 that cold-hardened material is subjected to significant influence of liquid mercury when testing under cyclic load. Comparing Figs. 117 and 115 where the fatigue tests of annealed 70/30 brass are given, we come to the conclusion that the degree of mercury effect in both cases is about the same. The effect of liquid metal on the annealed and cold-hardened materials is also similar: the effect decreases with decreasing amplitude of stress and has a minimum value in the region of the true endurance limit.

It follows from the comparison between Fig. 115 and 117 that the preliminary plastic deformation leads to the increase in fatigue strength of the material both in air and in liquid metal. Thus, the results in Ref. [289] indicate that cold-hardening does not cause a substantial change in the degree of influence of the liquid metal medium on the fatigue strength of the material and consequently is conducive to strengthening of the material about the same as when testing in air.

A similar conclusion also follows from Ref. [291] in which the results of bending tests of wire specimens of St. 40 as received and in the annealing state are given. Although the overall cold-hardening of the material does not affect the degree of decrease of fatigue strength of a solid metal in a liquid substantially, local plastic deformation may, however, noticeably decrease the effect of the liquid metal. This effect was observed by V. F. Karpenko during the cyclic bend test of L62 brass and D1 Duralumin [294]. He asserted that liquid mercury causes a decrease in the endurance of these materials, however its adverse effect is significantly weakened after rolling the surface of the specimens. The positive influence of surface cold-hardening in this case is determined apparently not by plastic deformation but by a secondary effect. It is well-known that deformation of specimens by rolling leads to residual compressive stresses in the surface layer of the metal [295]. These stresses may be appreciable, for example, in steel specimens they reached $50-70 \text{ kg/mm}^2$. The appearance of compressive residual stresses in the surface layer leads to the increase of specimen's endurance due to a decrease in the active stress amplitude. The rolling of surface defects in the structure appears to be also one of the factors promoting the decrease of the effect of liquid metal on the fatigue strength of rolled specimens [294].

c. Influence of stress concentrators

It has been determined by cyclic bend tests that the material subjected to the effect of liquid metal when testing smooth specimens experience its effect also when testing specimens with notches.

Fig. 118a shows the fatigue strength curve of St. 50 at a temperature of 400° C in air and in the melt of eutectic Pb-Bi [296].

Experiments were carried out with symmetrical bending of specimens at a frequency of 50 cycles/sec. Smooth cylindrical specimens and specimens with a circumferential notch 0.5 mm deep (working area 16 mm in diameter), radius at the tip of about 0.05 mm and an angle of 45° were tested.

It is evident from Fig. 118a that the liquid metal causes a decrease in the endurance of both smooth and notched specimens. The nature of the fatigue curve as a result of effect of liquid metal on the material does not change. If the smooth specimens when tested in air do not develop a true endurance limit then it is also absent when testing the specimens in liquid metal. The true endurance limit in specimens with stress concentrators was also observed in the inactive and active medium. The degree of the liquid metal effect on specimens with stress concentrators is greater than on smooth specimens based on the magnitude of the ratio of endurance limits in liquid metal and in air.

It has been determined by fatigue tests of specimens of 1Kh18N9T steel with circumferential notches under symmetrical bending that this material at a temperature of 500° C does not have a true endurance limit [297].

Its fatigue strength curve in coordinates of stress amplitude (the number of cycles to failure) develops a break in the region of small stress amplitude but in this case the right branch of the curve retains a certain slope towards the abscissa, i.e. the number of cycles to failure is finite under any load (Fig. 118b). The fatigue strength curve of 1Kh18N9T in the medium of liquid eutectic Pb-Bi has the same shape, however it falls below the curve corresponding to the testing in air. It should be noted that the endurance curves in air and in molten metal diverge after bending, i.e. the effect of the medium in this case increases continuously with the decreasing stress amplitude.

It is obvious that fatigue strength curves in Fig. 118 do not indicate all kinds of possible material endurance both in the inactive medium and in the aggressive liquid metal when testing specimens with stress concentrators. Although there are no pertinent experimental data, it follows from the general presentations on the effect of the medium that there is a possibility when (for example during corrosion action) the material has a true endurance limit in air and not in liquid metal.

d. Strengthening during the formation of intermetallic surface layer

The effect of the liquid metals does not always cause a decrease in fatigue strength of solid metals. As shown by M. I. Chayevskii the endurance of the material in liquid metal medium is increased in some cases [298-303]. This effect was observed during cyclic deformation of carbon steels and chromium nickel austenitic 1Kh18N9T steel in liquid

tin and eutectic Pb-Sn.

Fig. 119 shows the fatigue strength curve of St. 50 under symmetrical bending in air and in the eutectic Pb-Sn. The experiments were carried out on cylindrical specimens, smooth and with circumferential notches. The test temperature in all cases was 400° C. It is evident from Fig. 119 that under the action of eutectic Pb-Sn the fatigue strength of steel increases.

The strengthening action of the liquid metal appears when testing smooth specimens and specimens with stress concentrators. The degree of strengthening of the latter however is greater. Thus, the maximum increase of the arbitrary endurance limit in liquid metal reaches 60% when testing specimens with stress concentrators and only 12% in smooth specimens.

A similar ratio of magnitudes of strengthening effect of smooth and specimens with notches was also observed when testing other types of carbon steels and 1Kh18N9T steel.

M. I. Chayevskii established that the increase in fatigue strength of materials is determined by the formation of an intermetallic layer on the specimen's surface. In case of steel in contact with tin or eutectic Pb-Sn the intermetallic compound FeSn_2 is formed. The FeSn_2 lattice is larger than that of Fe. For this reason compressive stresses arise in the newly formed surface layer.

The existence of compressive stresses was confirmed by M. I. Chayevskii who carried out experiments with steel plates. The steel

plate surface was coated with a liquid metal. The heating of these plates is accompanied by the growth of an intermetallic layer resulted in their bending [302]. Compressive stresses in the surface layer were also determined quantitatively [303] by the method of cutting ring specimens developed by N. N. Davidenko. It was found that holding a steel container with molten tin at a temperature of 400° C for 73 hrs causes the appearance of compressive stresses of up to 20 kg/mm².

The origination of compressive stresses in the surface of the specimens during the interaction with liquid metal is also confirmed by the fact that greater strengthening occurs in notched specimens than in smooth ones. These effects were also observed when testing specimens having compressive stresses due to surface cold-hardening in air [295].

The strengthening action of tin and eutectic Pb-Sn on steel under cyclic straining is not observed at any temperature. The experiments have indicated that with the increase of temperature the strengthening effect decreases and subsequently gives away to the effect of decrease in fatigue strength. For example, it has been established by testing specimens of St. 35 with stress concentrators that the endurance limit based on 2×10^7 cycles at a temperature of 250° C in the medium of eutectic Pb-Sn exceeds the limit at the same number of cycles and temperature in air by a factor of one and a half [301]. The increase of test temperature leads to the continuous decrease of ratio of these limits so that beginning with 500° C it becomes less than unity, i.e. endurance

of steel in eutectic Pb-Sn at this temperature becomes lower than endurance in air. The corrosive action of liquid metal at high temperatures can be explained in this case by the intensive dissolution process [301].

The strengthening effect of steels during fatigue tests in tin and eutectic Pb-Sn is observed when loading specimens not only by bending but also by torsion. However, under the second type of loading the degree of strengthening is lower than under the first. This difference becomes clear when it is considered that the formation of a surface layer with compressive stresses by any method (for example, rolling) leads to much lower strengthening during cyclic twisting than during bending in air.

The strengthening effect of liquid eutectic Pb-Sn on St. 50 is intensified during cyclic twisting as shown in the experiment of [296], if the specimen was aged in liquid metal. The specimens were at first loaded with a stress of 15 kg/mm^2 , which was subsequently increased in stages by $0.3\text{-}0.5 \text{ kg/mm}^2$ at 10 min intervals up to the ultimate testing value. It was found that aging in liquid metal causes an increase in the endurance limit of St. 50 by 40% and in an air medium only by 10%. It is possible that during this aging a significant role is played by the increase in soaking time of specimen in liquid metal for small stresses when there is not fatigue damage and the thickness of the intermetallic layer increases. Data on the smaller increase of fatigue strength of steel in eutectic Pb-Sn if the specimens are not previously coated

indicate the important role of time in the experiments under consideration [296, 303]. The decrease in fatigue strength of specimens with notches occurs in the eutectic at a large stress amplitude (see Fig. 119) and increase in endurance with a decreasing loading frequency [222].

Examination of Fig. 119 indicates that the strengthening during fatigue tests in eutectic Pb-Sn should disappear at a given number of cycle to failure exceeding the experimental data. This action of liquid metal is apparently associated with the fact that the intermetallic layer after reaching a certain thickness fails. A more durable strengthening during cyclic torsion may be achieved by adding aluminum into liquid lead alloys with tin. The experiments on St. 50 and 20Kh steels showed that additions of 3.8% Al to liquid metal promoted the increase of its strengthening action. This is also associated with the formation of a surface layer of intermetallic compound. In the Fe-Al system several intermetallic compounds are known: FeAl_3 , Fe_2Al_5 , FeAl_2 , FeAl and Fe_3Al [119]. Possibly one or several of them form the surface layer on steel during cyclic straining. The presence of this layer was confirmed by microstructural analysis of specimens during fatigue tests [223, 304]. In view of the layer cracking on the specimens subjected to long-term tests and also in view of its intensive growth at high temperatures the method of strengthening by introducing aluminum into eutectic Pb-Sn is apparently useful for a short time.

e. Damage to metal in the process of cyclic load

In the preceding section of the present chapter the total effect of liquid metal on the solid in the process of cyclic straining of the latter which was expressed by the decrease of a number of cycles to failure was evaluated. However, the effect of the medium on the metal during deformation is a continuously developing process. Therefore for each stage of cyclic straining the influence of liquid metal leads to some damage to the solid metal which is continuously intensified with an increasing number of cycles.

This nature of liquid metal effect on a solid during cyclic straining was confirmed by the results in Refs. [305-308]. The mechanical properties during fracture of specimens subjected previously to a thermal fatigue test for a period of a different number of cycles were determined. The test was carried out on wire specimens which were periodically heated (by passing an electric current through them) and cooled. The duration of heating was 8 sec, and cooling 17 sec. An abrupt change in temperature led to the origination of thermal stresses in specimen. Periodic oscillations of these stresses caused the appearance of lateral cracks in the surface layer of specimens coated with liquid metals. In specimens coated with a liquid metal there were no cracks even at a maximum number of cycles, such as 1000.

The formation of cracks and other microdefects in the metal structure during cyclic straining was due to the decrease of its strength and

ductility which was established by tensile tests of specimens with a constant deformation rate. Fig. 120 shows the dependence of damage to annealed nickel coated with bismuth on the number of cycles to deformation. In order to prevent damage caused by liquid metal effect the ratio of difference in strength of coated and uncoated specimens to strength of uncoated specimen was used. The mechanical properties of the metal not subjected to the action of the medium should be taken into account because cyclic straining also damages the uncoated metal. As evident from Fig. 120 the damage to nickel under the action of liquid bismuth is continuously intensified with an increasing number of cycles.

A similar influence was also obtained when testing copper, L62 brass and phosphor bronze with tin and other type coatings. The influence of the effect of liquid metal with the increase of the upper temperature of the cycle and lower constant temperature has been determined, i.e. with the increase of thermal stresses. The decrease of the effect after a given number of cycles or beginning with a certain upper temperature and with their further increase has been noted in certain cases. This result can be associated with some of the peculiarities of physico-chemical interaction between liquid and solid metals as well as with the oxidation of the coating since the experiments were carried out in air.

Table 13. Values of limiting crystallographic shear
during brittle fracture of zinc single crystals on basal plane

Specimens coated with mercury, temperature 20° C		Specimens without surface coating, temperature -196° C	
α_0	ϵ_c	α_0	ϵ_c
13	0.33	21	0.74
27	0.28	36	0.60
32	0.20	43	0.24
48	0.17	56	0.13
61	0.09	72	0.08
		76	0.04

Table 34. Mechanical properties of steel type St. 7 tested in uniaxial tension and torsion at 350° C

Environment	Tension		Torsion	
	Strength kg/mm ²	Relative elongation, %	Strength, kg/mm ²	Relative elongation, %
Air	90.0	20.5	33.8	41.9
Tin	57.4	1.2	34.1	40.8

Table 35. Mechanical properties of 30KhGSA steel in air and coated with tin at a temperature of 270-280° C

Thermal treatment of steel	Uncoated specimens			Specimens coated with tin		
	σ_B	δ_s , %	ψ , %	σ_B	δ_s , %	ψ , %
Hardening in oil, tempering at 350°C for a period of 1 hr	165.9	13.3	58.3	115.2	1.5	2.0
Hardening in oil, tempering at 500°C for a period of 1 hr	121.0	10.7	52.0	96.2	2.7	7.9
Annealing	66.4	12.3	30.2	63.6	11.3	25.4

Table 36. Mechanical properties of coarse-grained metals wetted locally with liquid metal

Solid metal	Liquid metal	Temperature, °C	Wetted surface*	Yield point, kg/mm ²	Yield strength, kg/mm ²	Relative elongation, %
Fe-3% Si, cast	Li	200	1	23.8	32.7	20.0
			2	23.4	24.0	1.6
			3	23.6	25.3	1.6
			4	24.3	29.8	7.0
70/30 brass cast	Hg	20	1	5.1	17.7	42
			2	4.6	5.0	2
			3	3.9	6.1	8
			4	5.1	17.4	43
Al-6% Mg, cast	Hg	20	1	6.6	10.1	3
			2	-	5.7	0
			3	-	4.9	0
			4	7.1	8.0	1
Cu, cast	Bi	300	1	3.1	11.0	24
			2	3.0	7.5	8
			3	-	**	-
			4	-	**	-
Cu, wrought	Bi	300	1	5.7	5.7	20
			3	3.2	8.0	4
			4	-	**	-
Al-4% Cu, wrought and aged	Hg	20	1	8.6	29.2	14.5
			3	14.9	20.5	6
			4	12.6	19.7	7

*1 - unwetted specimens; 2 - large area of the surface wetted (grain boundaries and grains); 3 - grain boundary wetted only; 4 - grain center wetted only.

**Specimens failed ductilely outside the wetted area.

Table 37. Mechanical properties of copper single and bicrystals
in the presence of bismuth at 350° C

Specimens tested	Angle between the grain boundary and tension axis, deg	Yield strength, kg/mm ²	Relative elongation, %	Relative reduction in area, %
Single crystals	-	9.41	45	60
		8.15	45	50
Polycrystals	-	4.86	-	-
Bicrystals	90	1.41	-	-
	60	2.04	5	-
	45	2.82	10	10
	30	4.70	25	10
	10	3.63	30	20
	0	8.94	40	40

Table 38. Influence of test temperature on mechanical properties of steels

Material	Temperature, °C	Specimens coated with tin			Specimens without coating		
		σ_B , kg/mm ²	δ , %	ψ , %	σ_B , kg/mm ²	δ , %	ψ , %
30KhGSA steel (hardening in oil, tempering at 500°C for 1 hr)	270-280	96.2	9.7	7.9	121.0	10.7	52.0
	400	22.0	0	0	105.0	13.2	36.7
	500	25.0	0	0	86.0	14.8	77.8
40KhGSA steel (annealing)	270-280	75.5	20.0	66.3	74.0	21.2	67.3
	400	68.7	6.4	11.0	70.5	22.7	69.0
	500	46.0	2.0	6.0	59.8	19.1	72.0
EI388	270-280	73.3	33.3	50.5	70.4	30.8	54.3
	400	66.5	26.0	29.2	72.0	33.5	51.0
	500	58.5	18.8	24.1	71.5	38.0	38.2

Table 39. Work of rupture during static and dynamic bending of notched specimens of 30KhGSA steel at a temperature of 300° C

Thermal treatment of steel	Surface coating	Work of rupture, kgm	
		static bending	dynamic bending
Hardening in oil, tempering at 300°C for 1 hr	- Sn	22.3 0.35	14.3 13.9
Hardening in oil, tempering at 500°C for 1 hr	- Sn	19.5 0.97	28.9 26.5

Table 40. Influence of deformation rate on mechanical properties of copper at room temperature

Grain diameter, mm	Coating	Deformation rate, %/hr	Yield strength, kg/mm ²	Relative elongation, %	Grain diameter, mm	Coating	Deformation rate, %/hr	Yield strength, kg/mm ²	Relative elongation, %
0.03	Hg	0.2	19.7	34.5	0.1	Hg	0.2	19.0	20
		40	20.0	36			40	17.6	22
		1000	22.2	44			1000	20.4	30
	Uncoated	40	21.3	50		Uncoated	40	19.4	42

Table 41. Mechanical properties of L68 brass at room temperature

Medium	Specimens without stress concentrators				Specimens with stress concentrators				
	σ_B kg/mm ²	δ , %	ψ , %	s_k	σ_B kg/mm ²	δ , %	ψ , %	s_k	a_{eff}
Air	36.3	50.5	59.5	89.7	30.1	25.0	15.2	36.7	0.83
Mercury	16.5	7.0	10.0	18.6	16.3	9.0	8.0	18.4	0.99

Table 42. Influence of cold-hardening at 20° C on the magnitude of normal fracture stresses of zinc single crystals coated with mercury at 20° and uncoated at -185° C

Preliminary deformation (elongation), %	Normal fracture stress, kg/mm ²	
	Uncoated specimens	Specimens with mercury coating
0	1.8	0.8
50	2.6	2.0
150	4.8	4.2
300	7.6	5.2
450	9.6	5.4

Table 43. Strength of aluminum alloy 2024-T3 during constant rate tension of 2.5 mm/min in contact with amalgams of different composition

Composition of amalgams, wt. %	Maximum breaking load	
	kg	Per cent of ultimate load
Hg	3080	80
Hg+0.25% Zn	2580	67
Hg+0.5% Zn	2527	65.5
Hg+1% Zn	2560	66.5
Hg+2% Zn	2215	57.5
Hg+4% Zn	1910	49.5
Hg+8% Zn	2042	53
Hg+0.25% Ga	2660	69
Hg+1% Ga	1785	46
Hg+2% Ga	1005	26
Hg+4% Ga	893	23
Hg+8% Ga	870	22.5
Hg+1% Na	2700	70.1
Hg+1.5% Na	2913	75.6
Hg+2% Na	2802	72.7
Hg+0.25% Cd	2904	75.5
Hg+0.5% Cd	2990	77.6
Hg+1% Cd	2970	77.0
Hg+2% Cd	2994	77.9
Hg+4% Cd	2885	75.0
Hg+0.25% Sn	3300	85.6
Hg+0.5% Sn	3193	83.0
Hg+1% Sn	3825	99.2
Hg+2% Sn	3150	78.2
Hg+4% Sn	3665	95.0
Hg+0.25% Mg	3551	92.1
Hg+0.5% Mg	2795	72.6
Hg+1% Mg	2940	76.4
Hg+2% Mg	2800	72.7

Table 44. Values of relative elongation during fracture under testing conditions for long-term strength of copper, Armco-iron and EI612 steel

Material	Medium	Temperature, °C	Time to failure, hr	Relative elongation during fracture, %
Cu	Air	350	10	4.02
		350	21	5.11
		350	45	3.12
		350	181	4.34
		350	215	1.64
Cu	Bi	350	9	0.18
		350	74	0.28
		350	284	0.15
Armco-Iron	Air	500	4.5	10.37
		500	23	17.64
		500	45	11.03
		500	500	13.96
Armco-Iron	Zn	500	14	6.55
		500	40	4.32
		500	97	3.00
		500	364	4.03
EI612 steel	Air	1000	18	9.06
		1000	72	7.03
		1000	147	2.90
EI612 steel	Li	1000	10	4.16
		1000	46	2.37
		1000	315	0.81

Table 45. Results of long-term strength tests of EI612 steel in air and in convection flow of lithium

Temperature, °C	Medium	Long-term strength, kg/mm ² , for different time, hr		Ratio of long-term strength in lithium and in air for different time, hr	
		100	1000	100	1000
700	Lithium	19.5	14.0	0.87	0.82
	Air	22.5	17.0		
1000	Lithium	1.8	1.0	0.82	0.67
	Air	2.2	1.5		

Table 46. Values of relative elongation during fracture under testing conditions for long-term strength of specimens of EI869 alloys in liquid sodium and in air at a temperature of 750° C and a stress of 20 kg/mm²

Wall thickness of specimen, mm	Relative elongation during fracture in air, %	Relative elongation during fracture in Na, %	Wall thickness of specimen, mm	Relative elongation during fracture in air, %	Relative elongation during fracture in Na, %
0.15	0.03	0.13	1.0	1.47	0.33
0.25	0.07	0.12	1.5	2.99	0.68
0.50	0.38	0.15	2.0	4.14	3.41
0.75	1.59	-			

Table 47. Values of steady-state creep rate of zinc single crystals coated with tin (v_{st}) and uncoated (v)

Temperature, °C	Stress, g/mm ²	ϵ , %/min	v_{st} , %/min	v_{st}/ϵ
200	76	0.7	0.2	0.3
280	51	1.7	10.0	6.0
350	19	1.0	15.0	15.0

Table 48. Values of decrement coefficients of creep limits for EI927 alloy in liquid sodium and EI612 steel in liquid lithium

Material	Temperature, °C	Decrement coefficient of creep limit K_{on} at a creep rate, % hr	
		10^{-4}	10^{-3}
EI827	600	1.00	1.00
	750	0.79	0.86
	800	0.60	0.68
	900	0.18	0.35
EI612	700	0.86	0.95
	1000	0.80	0.81

Table 49. Results of bend tests for wire specimens of St. 40 in mercury and in air at room temperature

Radius of grip jaws, mm	Steel as delivered			Steel after annealing at 840° C		
	Number of bends in air,	Number of bends in mercury,	n_p/n_a	Number of bends in air,	Number of bends in mercury,	n_p/n_a
1.0	9.70	7.34	0.78	8.6	6.84	0.79
2.0	18.40	16.60	0.90	10.44	9.50	0.91
3.0	26.80	25.90	0.97	12.70	11.92	0.94

Table 50. Results of fatigue tests during symmetrical bending of steels and alloys in air and in liquid sodium

Material	Temperature, °C	Medium	Arbitrary fatigue limit, kg/mm ² , in air and in sodium based on cycles		
			10 ⁴	10 ⁵	10 ⁶
EI437B	700	Air	44.0	37.0	32.0
		Na	44.0	37.0	32.0
EI855	700	Air	26.0	22.5	19.0
		Na	26.0	22.5	19.0
EI850	700	Air	23.0	20.0	17.0
		Na	23.0	20.0	17.0
EI853	600	Air	24.0	21.0	18.0
		Na	24.0	21.0	18.0
15KhMA	500	Air	27.5	25.0	22.5
		Na	27.5	25.0	22.5

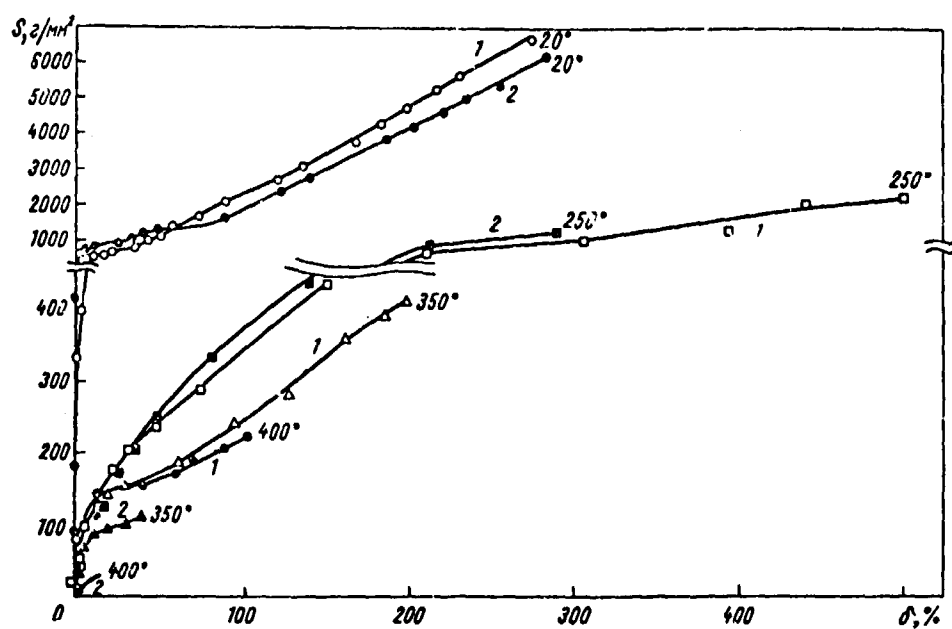


Fig. 72. Dependence of true stress S on the relative elongation of zinc single crystals uncoated (1) and coated with tin (2). The initial angle between basal plane and specimen's axis is 44° . The test temperature is shown on the graph.

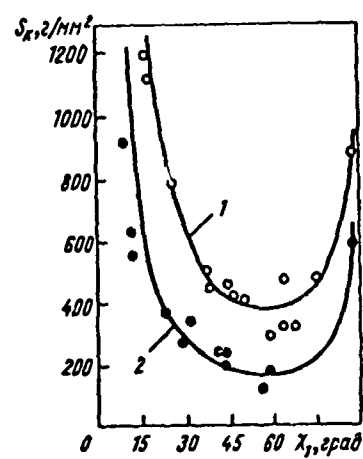


Fig. 73. Orientation dependence of true fracture stresses for zinc single crystal uncoated at room temperature of -196°C (1) and coated with mercury at room temperature (2).

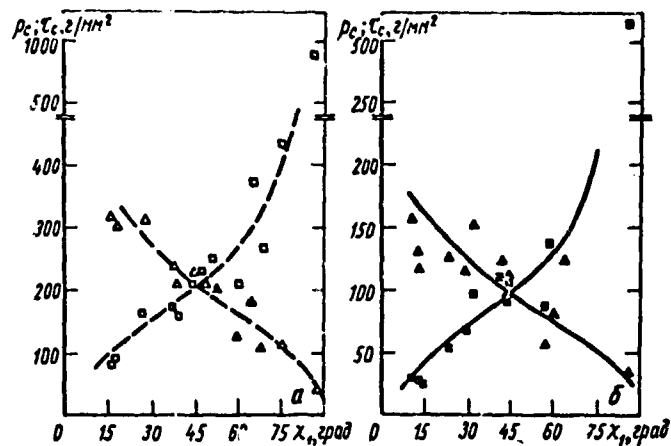


Fig. 74. Orientation dependence of normal p_c and shear τ_c stresses for zinc single crystals during fracture:

a - uncoated at a temperature of -196°C ;
b - coated with mercury at a temperature of 20°C
(χ_1 is the angle between basal plane and specimen's axis during fracture);

$\square, \blacksquare - p_c$;

$\Delta, \blacktriangle - \tau_c$.

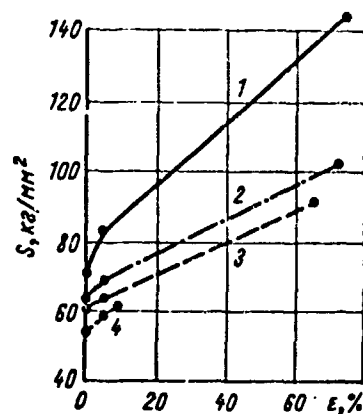


Fig. 75. Stress-strain curves for 30KhGSA steel after high tempering in air (1), in liquid bismuth (2), eutectic Pb-Bi (3) and alloy Pb-Sn (4) at a temperature of 500° C.

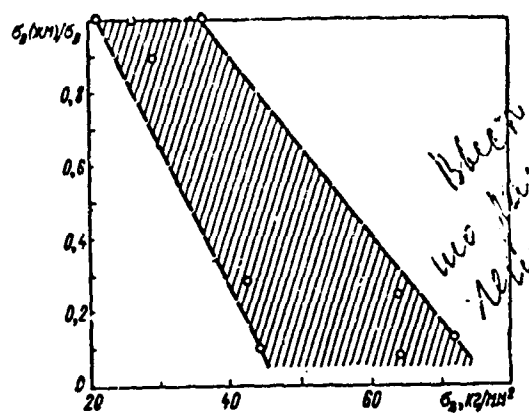


Fig. 76. Dependence of relationship between strength of aluminum alloys in liquid mercury and in air on the magnitude of initial strength (in air).

$\lambda_0 = 5,0$

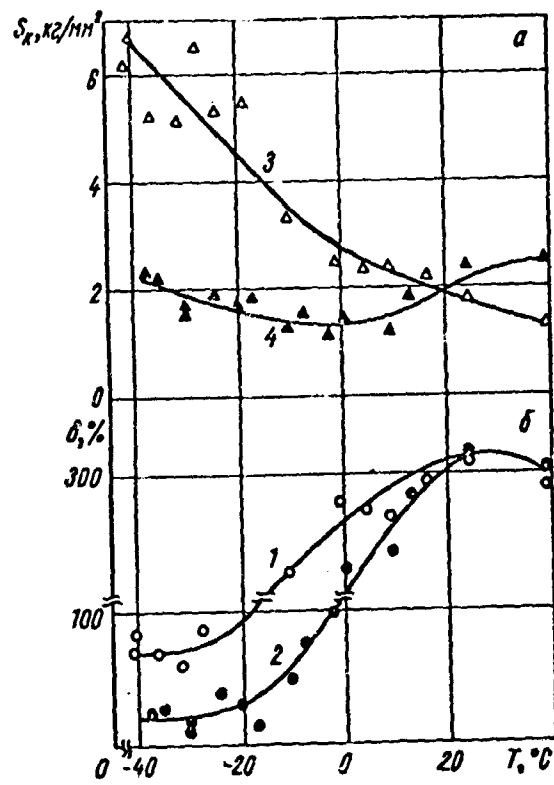


Fig. 77. Dependence of true strength (a) and elongation during fracture (b) on the temperature for pure (1, 3) and coated with mercury (2, 4) tin single crystals with .

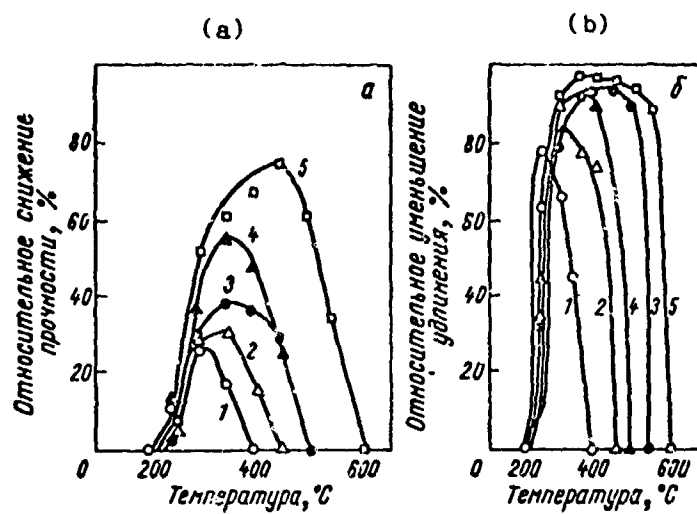


Fig. 78. Relative decrease of strength (a) and ductility (b) for steels in liquid tin as a function of temperature:

Carbon content: 1 - 0.05%; 2 - 0.35%; 3 - 0.55%; 4 - 0.73%; 5 - 1.08%.

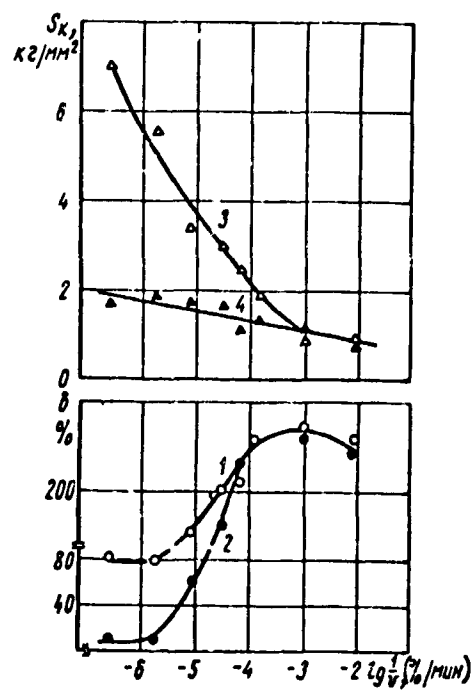


Fig. 80. Dependence of true strength and limiting relative elongation on the logarithm of reciprocal of deformation rate for pure (1, 3) and coated with mercury (2, 4) tin single crystals with $\chi_0 = 55^\circ$ at room temperature.

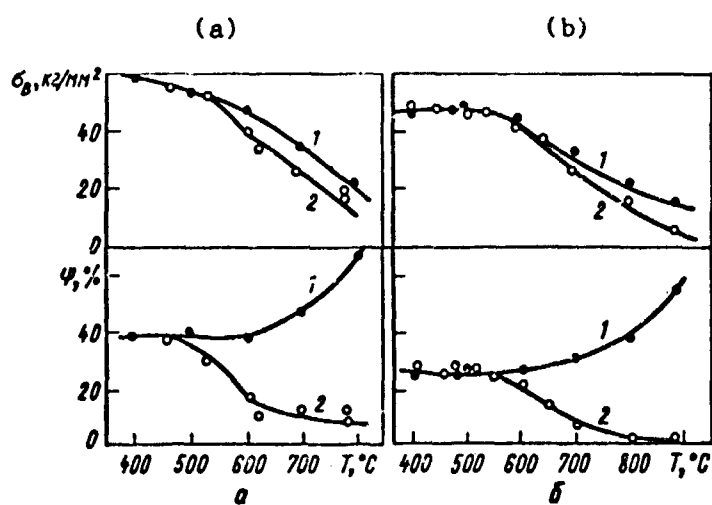


Fig. 79. Strength and relative reduction in area for EI878 (a) and 1Kh18N9T (b) steels at different temperatures:

- 1 - uncoated specimens;
- 2 - specimens coated with zinc.

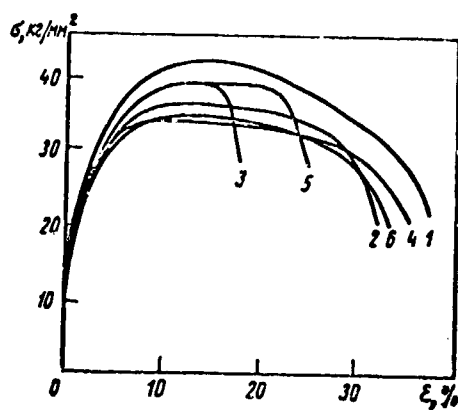


Fig. 81. Stress-strain curves for specimens of St. 20 tested at 400°C:

- 1 - testing in air at $v = 10$ mm/min;
- 2 - testing in air at $v = 0.055$ mm/min;
- 3 - testing coated specimens in a melt of eutectic Pb-Sn at $v = 10$ mm/min;
- 4 - testing coated specimens in a melt of eutectic Pb-Sn at $v = 0.055$ mm/min;
- 5 - testing coated specimens in a melt of eutectic Pb-Bi at $v = 10$ mm/min;
- 6 - testing coated specimens in a melt of eutectic Pb-Bi at $v = 0.055$ mm/min.

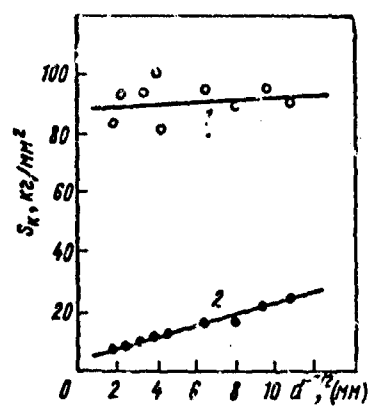


Fig. 82. Dependence of tensile strength of 70/30 brass on the average grain diameter at room temperature:

- 1 - uncoated specimens;
- 2 - specimens coated with mercury.

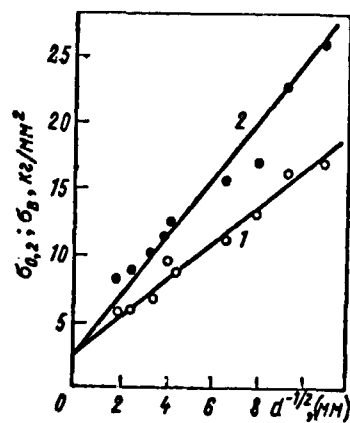


Fig. 83. Dependence of yield point (1) and true tensile strength (2) for 70/30 brass coated with mercury on the average grain diameter.

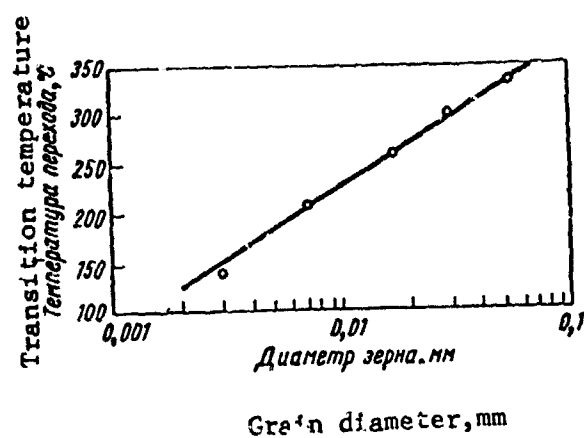


Fig. 84. Correlation between transition from brittle to ductile and average grain diameter for 70/30 brass wetted with mercury.

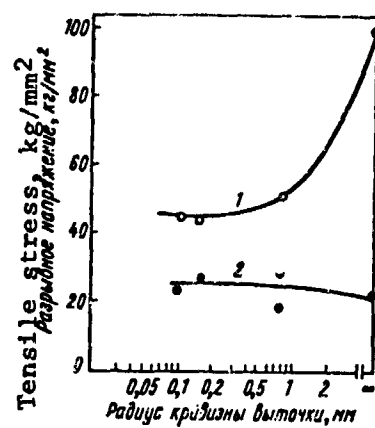


Fig. 85. Influence of stress concentrator in the form of a groove in the lateral surface of the flat specimen on the magnitude of tensile stress of aluminum alloy at room temperature:

- 1 - testing in air;
- 2 - testing in mercury.

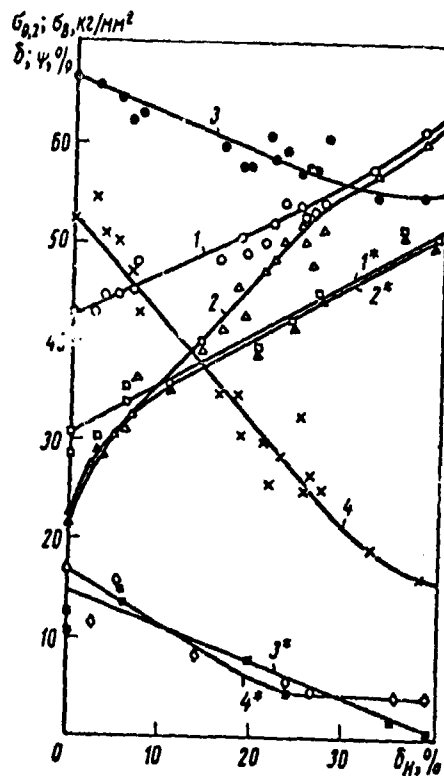


Fig. 86. Influence of cold-working by tension on the mechanical properties of L62 brass in air and in mercury at room temperature:

1 and 1* - strength;
 2 and 2* - yield point;
 3 and 3* - relative reduction in area;
 4 and 4* - relative elongation.

1, 2, 3, 4 - in air;

1*, 2*, 3*, 4* - in mercury.

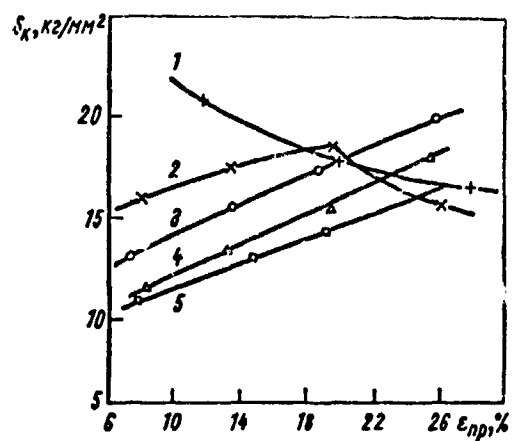


Fig.87. Dependence of true tensile stress of 70/30 brass coated with mercury on the degree of preliminary plastic deformation (ϵ_{np}) at room temperature:

Average grain diameter: 1 - 0.032 mm;
 2 - 0.08 mm;
 3 - 0.16 mm;
 4 - 0.275 mm;
 5 - 0.366 mm.

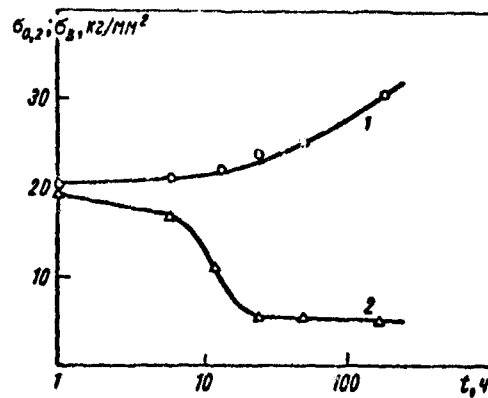


Fig. 88. Influence aging duration of aluminum alloy at room temperature after hardening in cold ($^{\circ}C$) water on its yield point when testing in air (1) and strength when testing in liquid mercury (2).

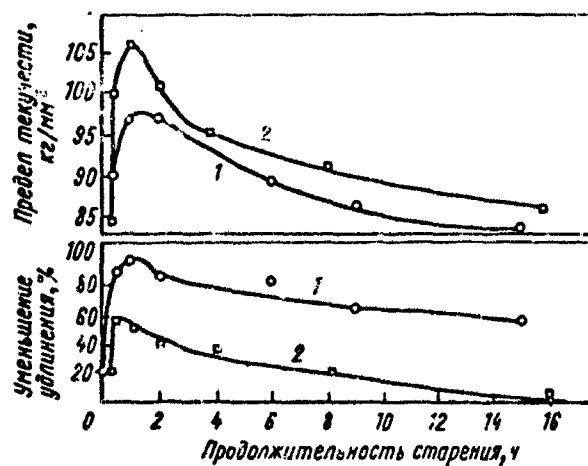


Fig. 89. Dependence of yield point and decrease of relative elongation of alloy Cu - 2% Be in contact with liquid metal (Hg - 2% Na) on the duration of aging at 370° C:

- 1 - hardened alloy;
- 2 - hardened and cold-worked.

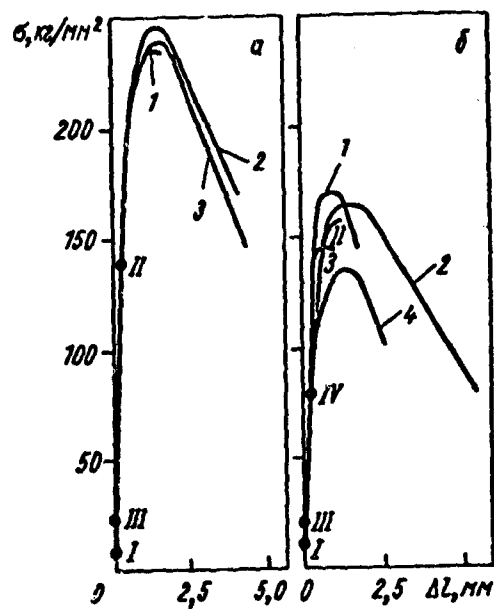


Fig. 90. Stress-strain curves for specimens of 40Kh steel with stress-concentrators after various thermal and thermomechanical treatments:

- a - testing at 400° C.
- 1, I - oil hardening at 850° C;
 - 2, II - thermomechanical treatment (TMT) by rolling;
 - 3, III - oil hardening at 850° C, rolling at room temperature.
- b - testing at 500° C.
- 1, I - oil hardening at 850° C;
 - 2, II - thermomechanical treatment by rolling;
 - 3, III - thermomechanical treatment with deformation by torsion (angle - 0.5 rad);
 - 4, IV - normalization, rolling at room temperature;
- 1, 2, 3, 4 - testing in air;
I, II, III, IV - test specimens coated with eutectic Pb-Sn.

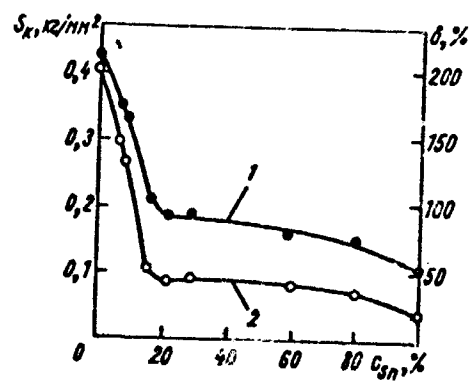


Fig. 91. Dependence of true tensile strength (1) and relative elongation during fracture (2) of zinc single crystals ($\chi_0 = 42^\circ$) on the tin concentration in Pb-Sn alloys at 350° C.

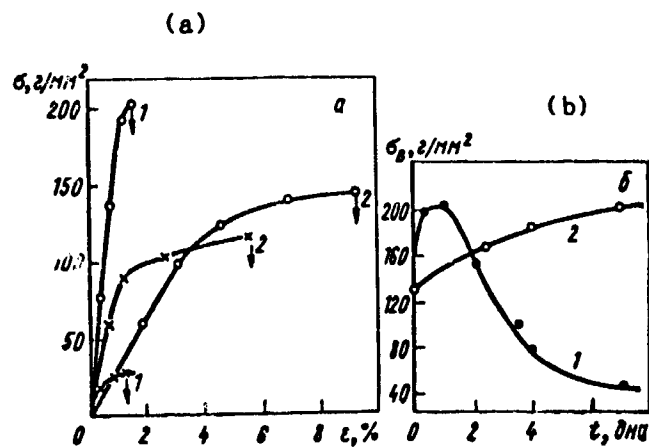


Fig. 92. a - Influence of electron irradiation on the deformation process of zinc single crystals ($\alpha_0 \approx 50^\circ$) coated with mercury. Single crystals after being amalgamated were exposed to 7 day (1) or to 15 min (2) irradiation and were stretched under irradiation:

- test specimens (nonirradiated);
- irradiated specimens.

b - Dependence of strength of amalgamated (1) and pure (2) zinc single crystals on the duration of preliminary electron irradiation.

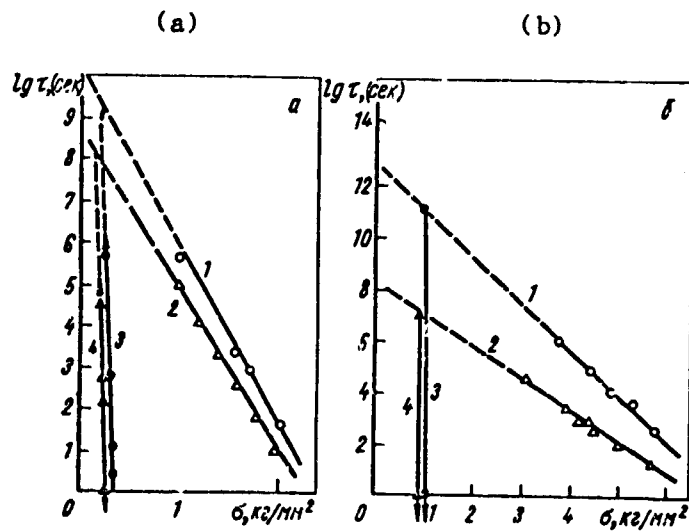


Fig. 93. Dependence of the time to rupture on the stress:

a - for zinc single crystals ($\alpha \approx 50^\circ$);

1, 2 - nonamalgamated specimens at 20 and 50° C respectively;
3, 4 - amalgamated specimens at those same temperatures;

b - for polycrystalline zinc;

1, 2 - nonamalgamated specimens at 20 and 100° C;
3, 4 - amalgamated specimens at those same temperatures.

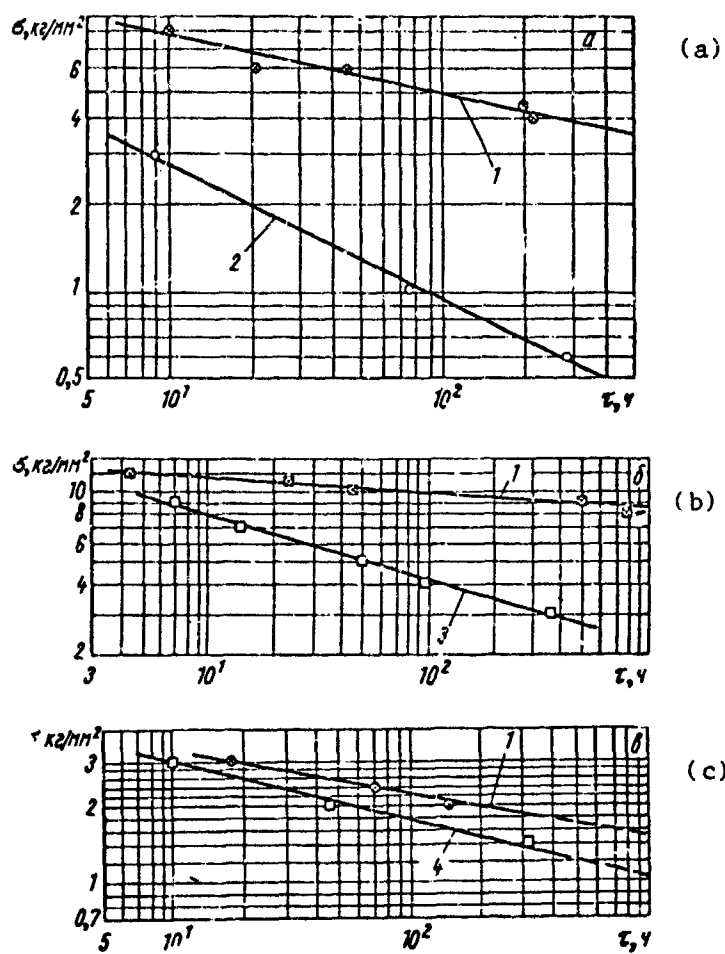


Fig. 94. Long-term strength curves for copper type M-1 at a temperature of 350° C (a), Armco-iron at 500° C (b) and EI612 steel at 100° C (c):

- 1 - testing in air;
- 2 - testing in bismuth;
- 3 - testing in zinc;
- 4 - testing in lithium.

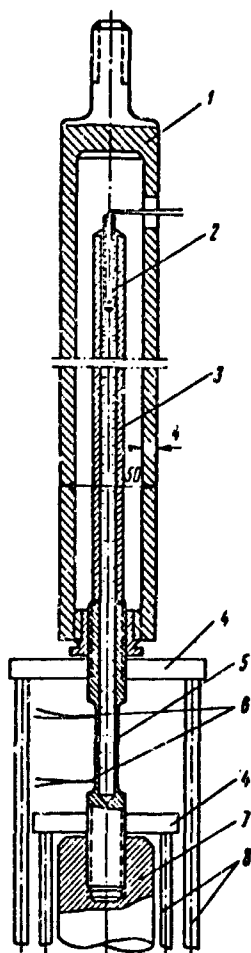


Fig. 95. Diagram showing the arrangement of the specimen in machine grips during long-term strength test in convection flow of liquid metal:

- 1 - upper grip;
- 2 - thermocouple pocket;
- 3 - elongation tube;
- 4 - crossarms of extensometer;
- 5 - specimen;
- 6 - thermocouple;
- 7 - lower grip;
- 8 - crossbar of extensometer.

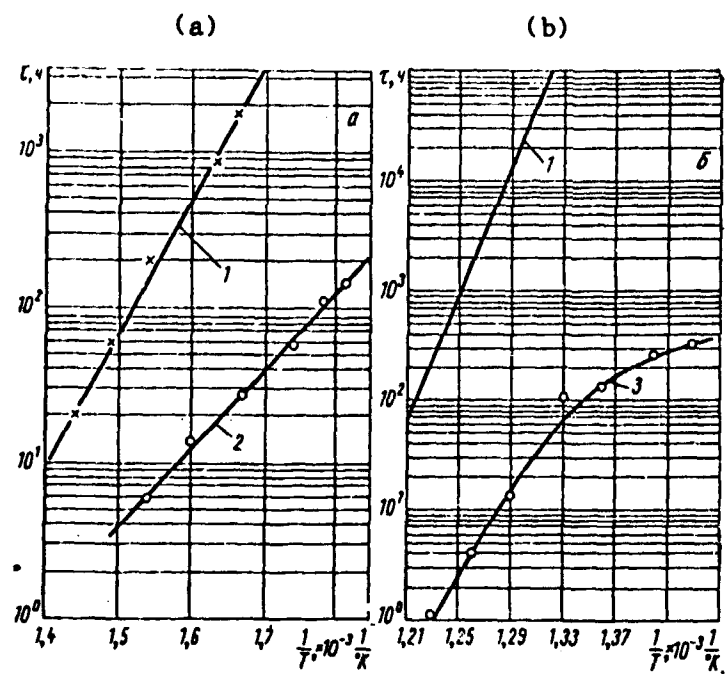


Fig. 96. Dependence of the time to rupture on the reciprocal of temperature for copper under a stress of 4 kg/mm² (a) and Armco-iron under a stress of 7 kg/mm² (b):

- 1 - testing in air;
- 2 - testing in liquid bismuth;
- 3 - testing in liquid zinc.

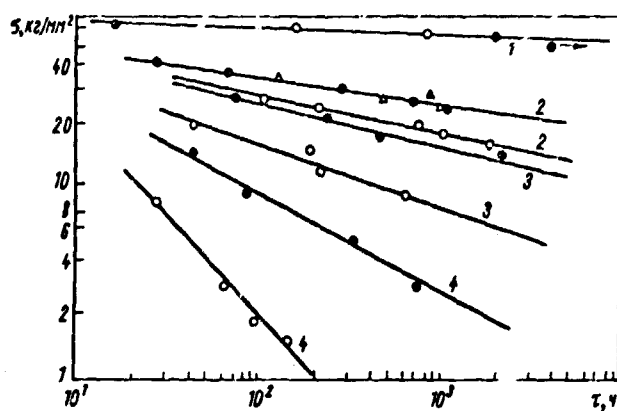


Fig. 97. Long-term strength curve for alloy EI827 at a temperature of 600 (1), 750 (2), 800 (3) and 900° C (4) in a convection flow of sodium (○) and in air (⊗).

Δ - testing in sodium under static isothermal conditions at 750° C.

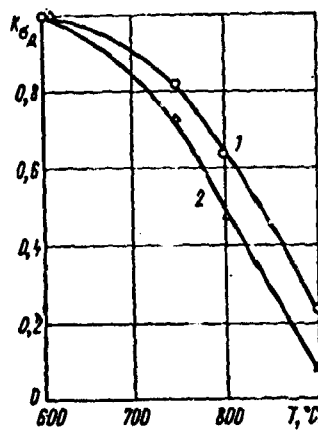


Fig. 98. Dependence on the temperature coefficient in decreasing the long-term strength of EI827 alloy in a convection flow of liquid sodium:

1 - $\tau = 100$ hrs;

2 - $\tau = 1000$ hrs.

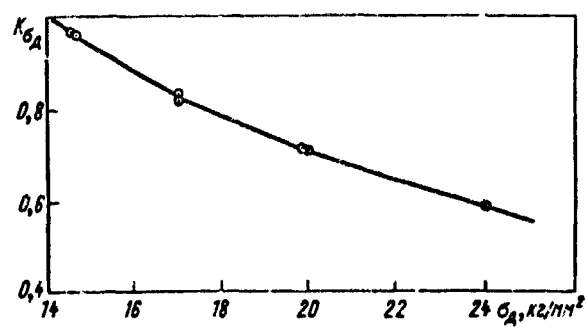


Fig. 99. Dependence of the coefficient of decrease of long-term strength of steels in liquid bismuth on the value of their strength in air.

Tests were carried out at a temperature of 700° C.

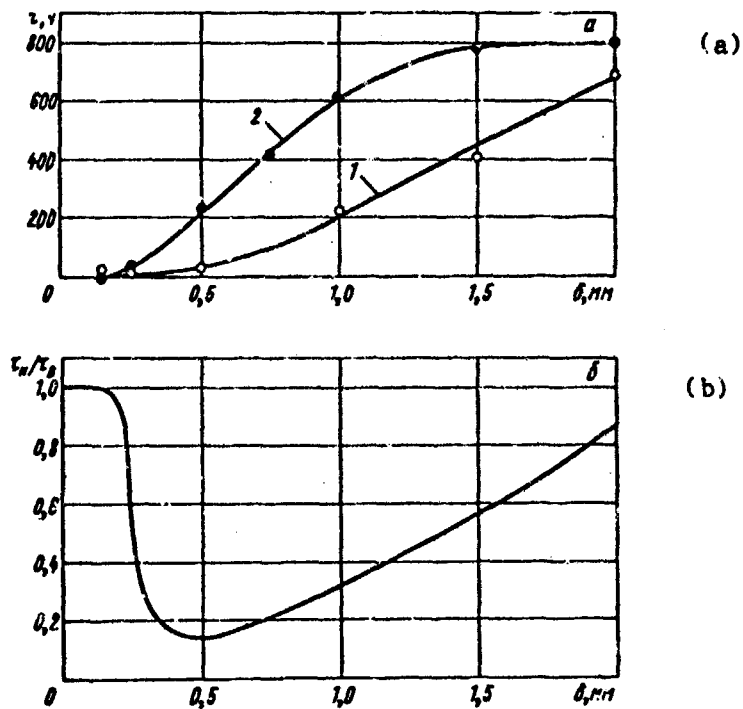


Fig. 100. a - Dependence of the time to rupture of specimens of EI869 alloy on the thickness of their walls during long-term strength test in liquid sodium (1) and in air (2) at a temperature of 750° C and under stress of 20 kg/mm².

b - Dependence of ratio of time to rupture in sodium to time to rupture in air on the wall thickness of specimens of EI869 alloy under those same test conditions.

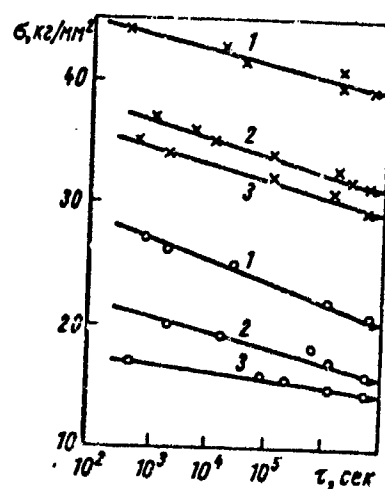


Fig. 101. Long-term strength curve for brass type LS59-1 in liquid mercury (○) and in air (X) at room temperature.

Average grain diameter: 50 microns (1);
220 microns (2);
280 microns (3).

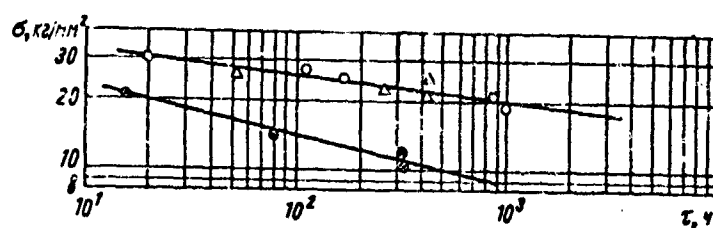


Fig. 102. Long-term strength curve for EI765 alloy at a temperature of 750° C:

- testing in air;
- testing in pure sodium (0.01% by wt. O₂)
- testing in sodium contaminated with oxygen (10% by wt. O₂).

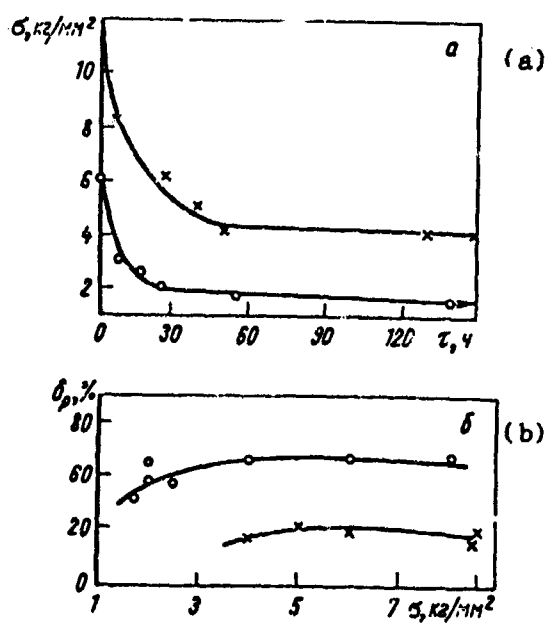


Fig. 103. a - Time dependence of strength for EI617 alloy at a temperature of 1000°C .

b. Dependence of limiting relative elongation on the stress during long-term strength test:

- testing in air;
- testing in unpurified sodium.

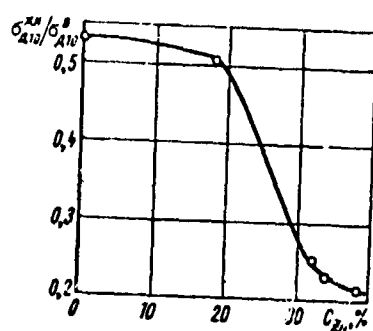


Fig. 104. Dependence of ratio of long-term strength after 10 hrs in liquid tin and in air on the zinc-content in brass. The test temperature was 240° C.

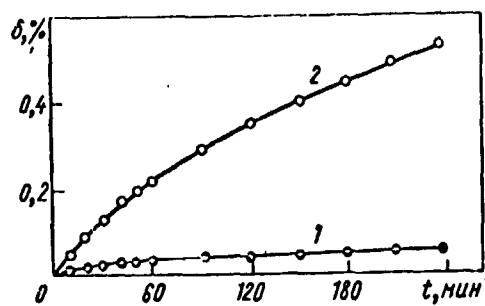


Fig. 105. Creep curves for pure zinc single crystals (1) and coated with tin (2) at a temperature of 350°C and under a stress of 19.1 g/mm^2 .

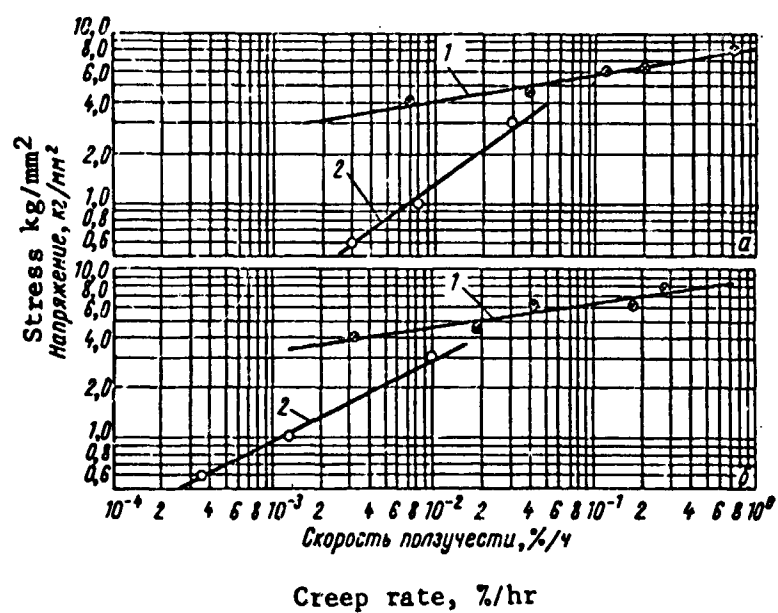


Fig. 106. Dependence of mean creep rate in the first stage (a) and steady-state creep rate (b) on the stress for copper in air (1) and in liquid bismuth (2) at a temperature of 350° C.

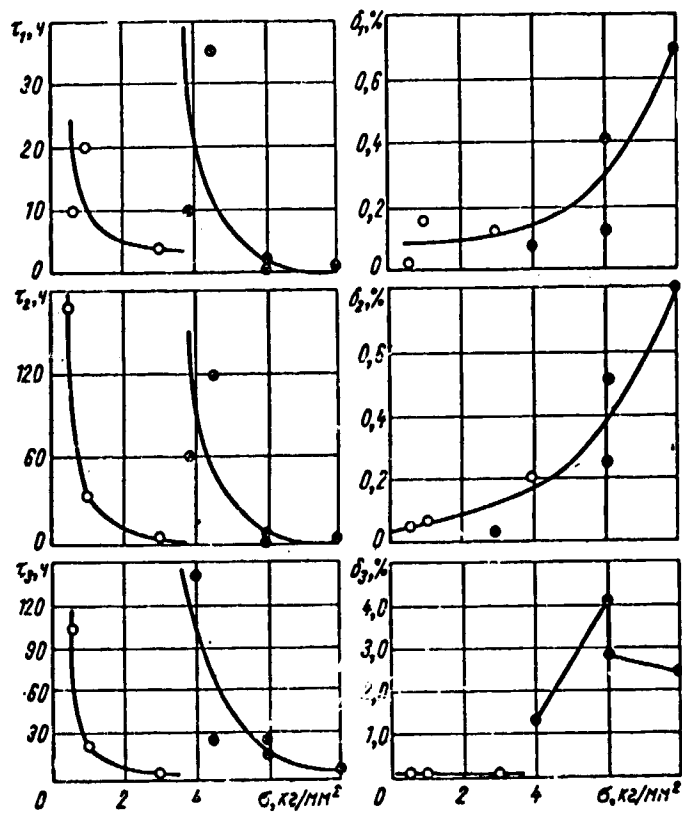


Fig. 107. Dependence of the duration of the first, second, and third stages of creep (τ_1, τ_2, τ_3) and relative elongation ($\delta_1, \delta_2, \delta_3$) on the stress for copper in liquid bismuth (\bigcirc) and in air (\otimes) at a temperature of 350°C .

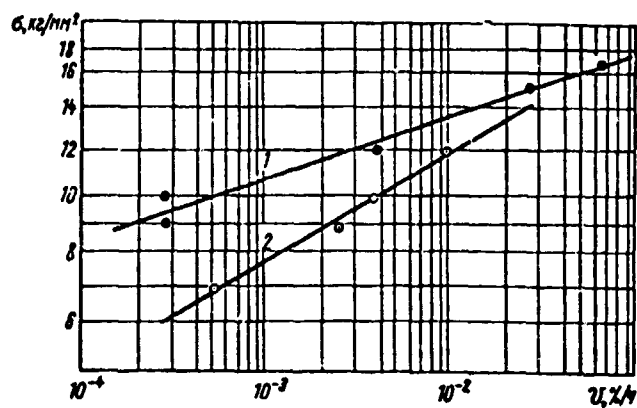
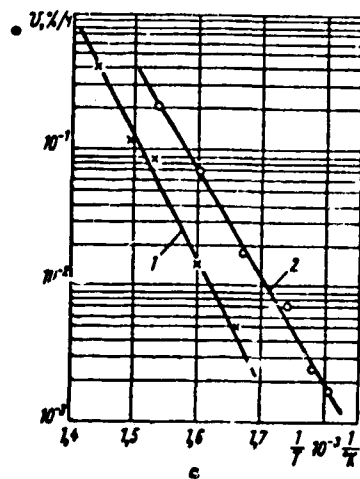
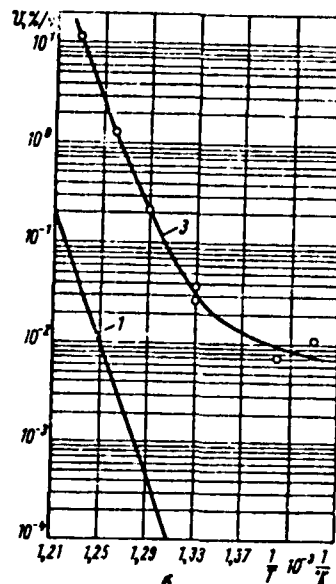


Fig. 108. Dependence of steady-state creep rate on the stress of 1Kh14N14MZB steel at a temperature of 700° C in air (1) and in a convection flow of liquid sodium (2).



(a)



(b)

Fig. 109. Temperature dependence of steady-state creep rate for copper under a stress of 4 kg/mm² (a) and Armco-iron under a stress of 7 kg/mm² (b):

- 1 - testing in air;
- 2 - testing in liquid zinc.

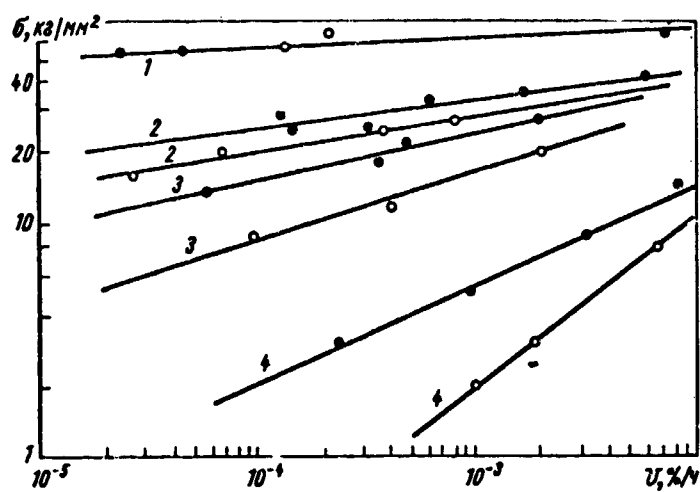


Fig. 110. Dependence of steady-state creep rate on the stress for EI827 alloy at a temperature of 600 (1), 750 (2), 800 (3) and 900° C (4) in air (\otimes) and in a convection of liquid sodium (\circ).

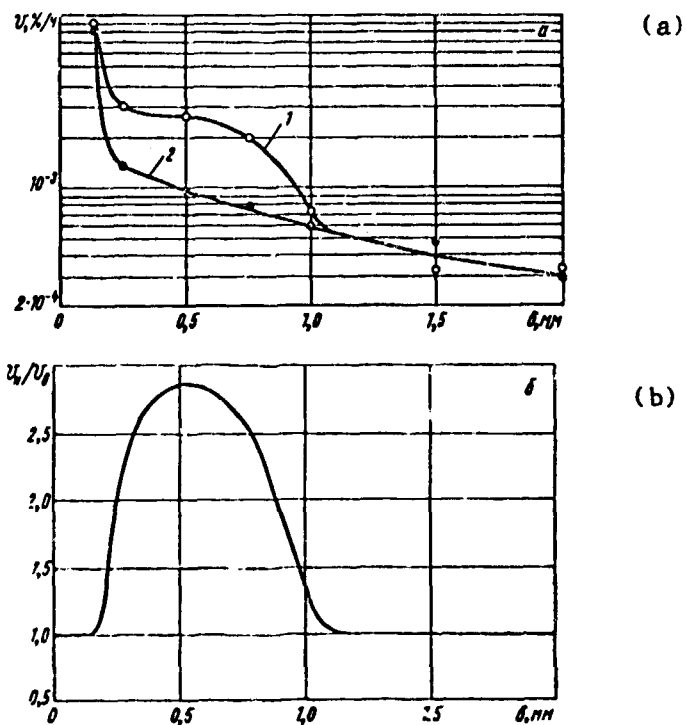


Fig. 111. a - Dependence of steady-state creep rate of specimens of EI869 alloy on the thickness of their walls when testing in liquid sodium (1) and in air (2) at a temperature of 750° C and under a stress of 20 kg/mm²;

b - Dependence of ratio of creep rate in sodium and in air on the wall thicknesses of specimens of EI869 alloy under identical experimental conditions.

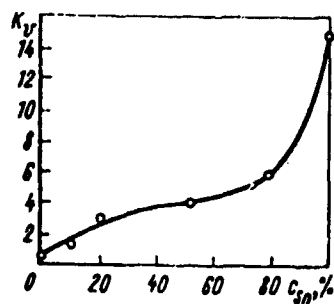


Fig. 112. Dependence of coefficient of decrease of steady-state creep rate of zinc single crystals in liquid metal on the tin content in alloys with lead.

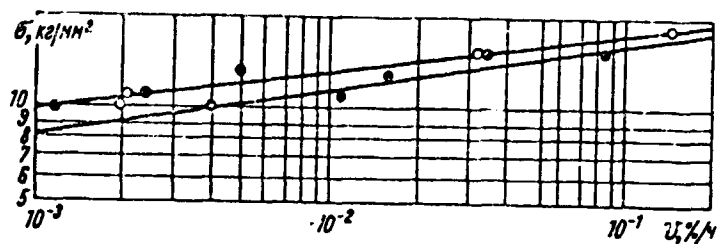


Fig. 113. Dependence of steady-state creep rate of EI851 steel on the stress at a temperature of 700° C:

- ⊗ - testing in air;
- - testing in pure sodium;
- ⊙ - testing in sodium contaminated with oxygen.

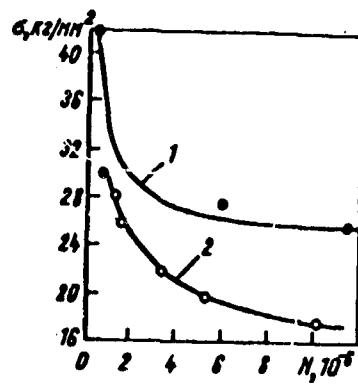


Fig. 114. Fatigue strength curves for EI617 alloy at a temperature of 700° C in air (1) and in liquid lead (2).

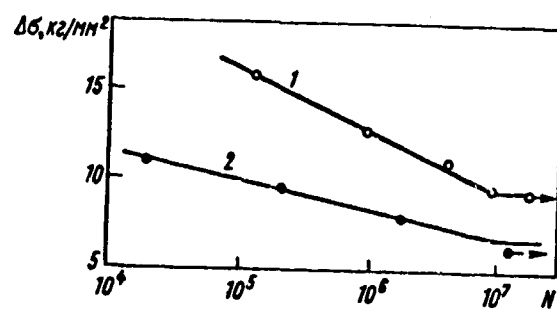


Fig. 115. Fatigue strength curve when bending annealed 70/30 brass at room temperature:

- 1 - specimens without surface coating;
- 2 - specimens coated with mercury.

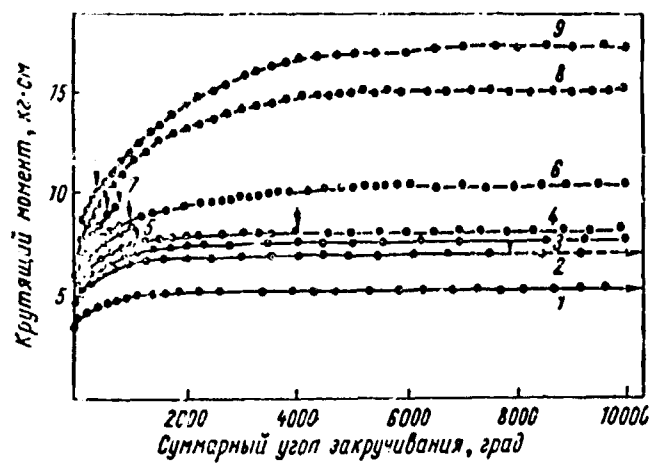


Fig. 116. Dependence of torque on the total angle of twist of 70/30 brass tested for fatigue in torsion at room temperature. Solid lines represent testing in mercury, broken lines represent testing in air.

Deformation amplitude: 1 - 1° ;
 2 - 3° ;
 3 - 4° ;
 4 - 5° ;
 5 - 7.5° ;
 6 - 10° ;
 7 - 15° ;
 8 - 20° ;
 9 - 40° .

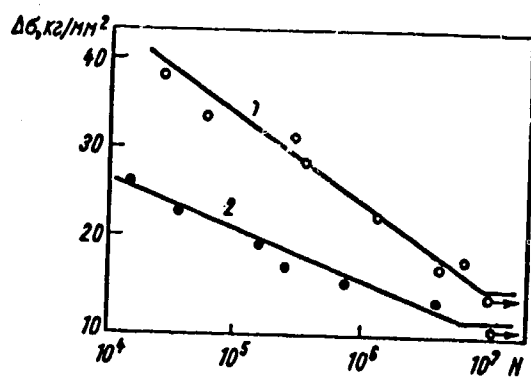


Fig. 117. Fatigue strength curve for cold-worked 70/30 brass bent at room temperature:

- 1 - specimens without surface coating;
- 2 - specimens coated with mercury.

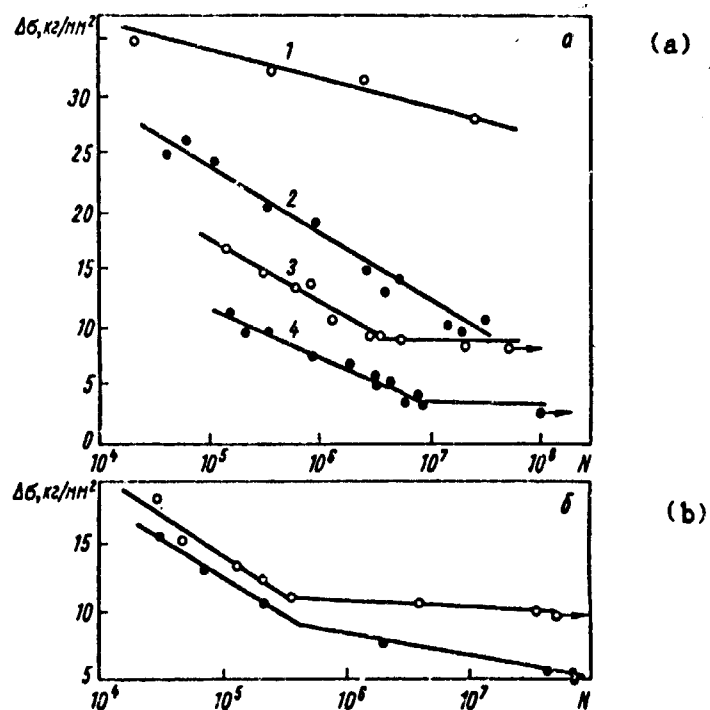


Fig. 118. a - Fatigue strength curve for normalized St. 50 bent at a frequency of 50 cycles/sec at a temperature of 400°C :

- 1, 2 - Smooth specimens;
- 3, 4 - Specimens with notches;
- 1, 3 - testing in air;
- 2, 4 - testing in eutectic Pb-Bi.

b. Fatigue strength curve for 1Kh18N9T steel bent at a frequency of 40 cycles/sec (hardening in water at a temperature of 500°C . Specimens with notches:

- - testing in air;
- - testing in eutectic Pb-Bi.

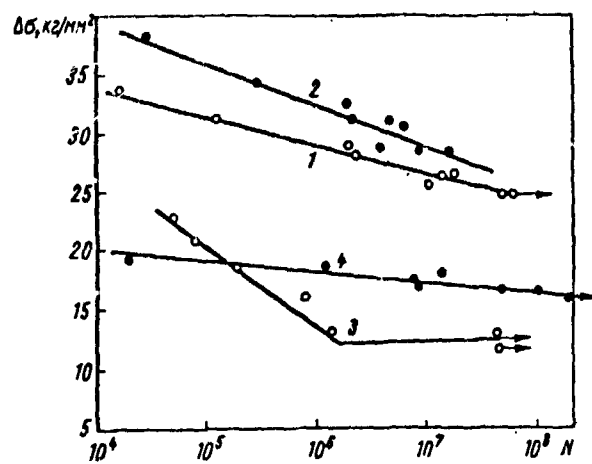


Fig. 119. Fatigue strength curve of normalized St. 50 under symmetrical bending at a temperature of 400° C:

- 1, 2 - Smooth specimens;
- 3, 4 - Specimens with circumferential notches;
- - testing in air;
- ⊕ - testing in eutectic Pb-Sn.

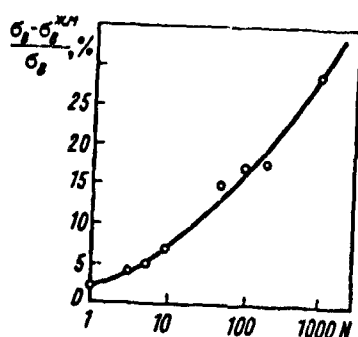


Fig. 120. Dependence of damage to nickel coated with bismuth on the number of cycles to deformation. Change in temperature when testing within 80-800° C.

PART II

CHAPTER 5

MECHANISM OF REACTION OF LIQUID METALS ON SOLIDS IN A STRESSED STATE

Three Factors Determining The Action of Liquid Metals

It was stated in the introduction to Chapter II of this book that the influence of liquid metals on solids during the process of deformation may result from three factors: adsorption, diffusion and corrosion. Certain effects related to the influence of each of these three were described in the preceding four chapters. The appearance of each factor was generally related to specific conditions of experiments, which were selected so as to demonstrate the action of the factor in question. It must be expected that in many cases, particularly when a material operates over an extended period of time, the influence of a liquid-metal medium may be the result of the influence of all three factors. It is therefore of interest to perform experiments which do not give preference to any of these factors, then eliminate each one in sequence, in order to determine the nature and relative share of the influence of each one individually.

It was decided to perform an experiment on the long term strength of armco iron in liquid zinc. As we know, zinc diffuses into iron even at relatively low temperatures [309-311], the diffusion of the zinc occurring at rather high speed. For example, according to the data of [310], at 500° C, zinc penetrates into iron to a depth of 75 μ and 10 min. We also know that iron is corroded in liquid zinc, primarily a result of its dissolution [312, 313]. It has been experimentally established that zinc wets iron [314]; consequently, it is an adsorption-active medium. Thus, the appearance of all three factors -- the adsorption, corrosion and diffusion factors -- is possible in principle as iron is deformed in liquid zinc.

Long term strength tests of armco-iron were performed at 500° C. Tubular machined specimens were used; the external diameter of the gauge section was 11 mm, the wall thickness was 0.5mm. After preparation, the specimens were annealed in a vacuum (about 10^{-4} mm Hg) at 600° C for five hours. During the test, the liquid metal was held in the internal cavity of the specimen. The internal volume was sealed by welding on a cap made of armco iron like the specimen. Before welding, the free space beneath the cap was blown through with argon. Specimens were tested for long term strength with monaxial extension using UIM-5 machines.

In order to determine the role of the adsorption, corrosion and diffusion factors in the overall effect of reduction of long term strength of the iron in zinc, four series of tests were performed. The specimens in the first series were used to test the properties of armco iron without the influence of the liquid metal. These specimens were not filled with liquid metal, but their internal cavity was sealed with a plug. The specimens of the second series was filled with zinc (TSV zinc was used). The testing of these specimens did show the change in long term strength of the iron under the simultaneous influence of the adsorption, corrosion and diffusion factors. The third series of specimens was filled with zinc saturated with iron. Saturation of the zinc was performed by holding it at 600° C for fifty hours in a tank made of armco iron containing iron filings. Thus, the corrosion effect of the liquid metal was eliminated in the third series of experiments and, consequently, the change in long term strength could have been caused only by adsorption effects and diffusion of zinc into the iron.

It should be noted that zinc forms intermetallic compounds with irons so that, strictly speaking, corrosion of the iron by zinc is related to dissolution and formation and intermetallides. However, since the formation of the layer of intermetallic compounds can only result in an increase in time to rupture of the specimen in the case of good bonding with the surface, as has been established for example in the testing of materials for fatigue (see Chapter IV, Section 4), only the process of dissolution of iron in the liquid metal should be considered in an analysis of the affect of decreasing long term strength as a result of the corrosion factor. It will be shown below that the bonding of the layer of iron-zinc intermetallides to the surface of the specimen was poor in the experiments. This allows us in this case to limit ourselves to consideration of the influence of the dissolution process alone.

Specimens used in the fourth series of experiments were filled with iron-zinc alloy powder, which did not melt at the

long term strength testing temperature of 500°C . The alloy was made (iron content about 1.5 weight %) so that its melting point was $600-650^{\circ}\text{C}$. Consequently, the wall of the specimen in this case contacted not liquid metal but a finely dispersed powder. Since the melting point was only slightly higher than the experimental temperature, and since it was well packed into the specimen, the powder is rapidly sintered, and the internal surface of the specimen becomes a boundary between two solid phases.* Obviously, the free surface energy of this boundary is higher than the energy of a solid iron -- liquid zinc boundary. Therefore, specimens of the fourth series should have greater long term strength than specimens of the third series. The increase in long term strength results from weakening of the influence of the adsorption factor.

The diffusion factor was present in the fourth series of experiments to the same extent as in the third series. Some difference was possible only with brief experimental time; as concerns specimens tested for ten or hundreds of hours, the diffusion influence of the medium was doubtless identical.

The results of long term strength tests are shown on Figure 21 in the form of the time to rupture as a function of stress. As can be seen from the graph, zinc is a highly corrosive medium in relation to iron. Whereas the tensile strength of armco iron after 1000 hours without the influence of the liquid metal is 8.5 kg/mm^2 , in zinc the strength is only 2.2 kg/mm^2 . The effect of the zinc on the armco iron is weakened by saturating the liquid metal with iron, that is by eliminating the influence of the corrosion factor. In this case, the long term tensile strength is 3.0 kg/mm^2 . Weakening the adsorption factor causes a further increase in long term strength of armco iron: the long term tensile strength determined in the fourth series of experiments was 3.6 kg/mm^2 .

In all cases, the influence of the medium increases with increasing test duration and correspondingly with decreasing stress applied to the specimen. An exponential dependence is observed between stress and time to failure for specimens in all series.

The affect of the zinc leads not only to a decrease in the total life time of specimens, but also to a decrease in all individual creep periods. (Figure 122). The greatest decrease in the lengths of the second and third creep periods is caused by the pure zinc.

* Sintering of the powder was noted in all specimens tested for long term strength; after rupture sintering was found to be practically independent of test duration.

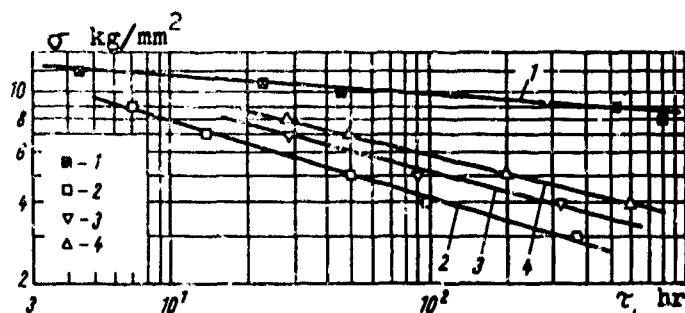


Figure 121. Diagram of long term tensile strength of armco iron at 500° C; tested in air (1) in pure liquid zinc (2), in iron-saturated liquid zinc (3) and in contact with solid iron-zinc alloy (4).

The relative elongation of the specimens as a result of the creep during the time to rupture is also reduced as a result of the zinc. Thus, whereas the elongation of specimens tested without zinc fluctuates between 10 and 18%, the relative elongation of specimens exposed to zinc lies between 2 and 10%.

The influence of the zinc is also manifested in an increase in the creep rate of the armco iron. We can see from Figure 123 that the rate of stable creep is most strongly increased in pure zinc, although the results for the pure medium and the iron-saturated medium correspond. Consequently, in this case elimination of the corrosion factor had no influence on the creep rate of the iron. The diffusion influence of zinc, as the results of tests in the fourth series of experiments show, also facilitates a rise in the creep rate of armco iron. The difference in the creep rates in air and in contact with zinc increases when the stress is decreased. An exponential dependence between applied stress and rate of stable creep is observed when specimens are tested in air and in contact with zinc. The regularities of a change in the stable creep rate are similar to the regularities of the change in average velocities of creep during the first and third periods.

Studies of the microstructures of the long term strength specimens after rupture showed that the influence of the zinc in all cases leads to an increase in the number of intercrystalline cracks. In specimens tested for extended periods of time, almost all grains in the surface layer are separated by cracks (Figure 124).

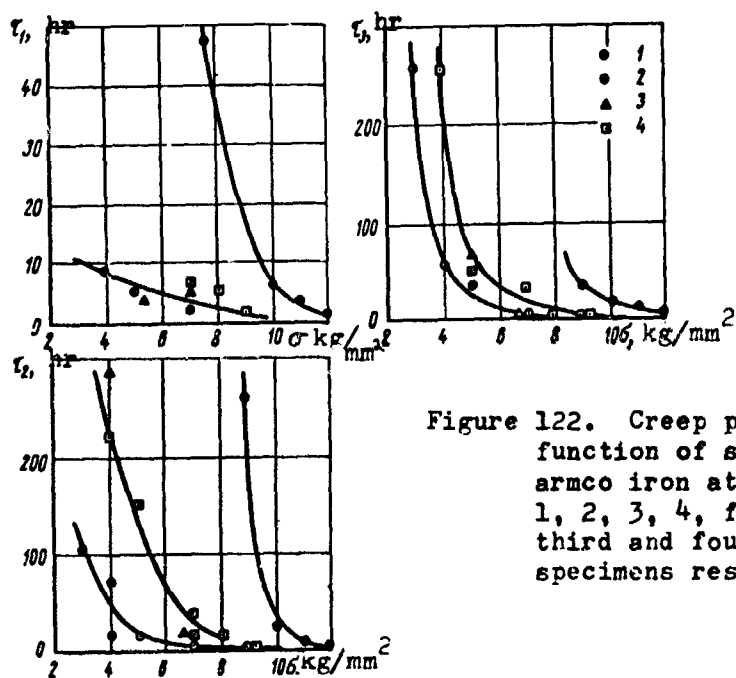


Figure 122. Creep periods as a function of stress for armco iron at 500°C : 1, 2, 3, 4, first, second, third and fourth series of specimens respectively.

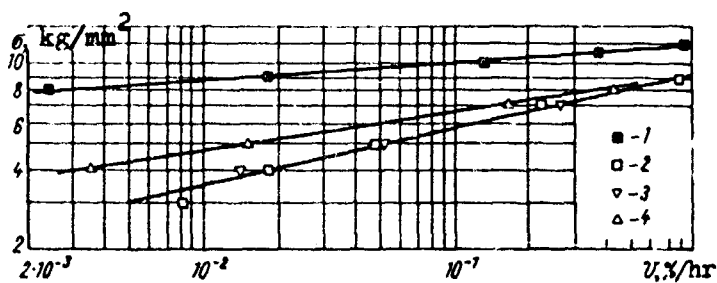


Figure 123. Stable creep rate as a function of stress for armco iron at 500°C : 1, 2, 3, 4, first, second, third and fourth series of experiments respectively.

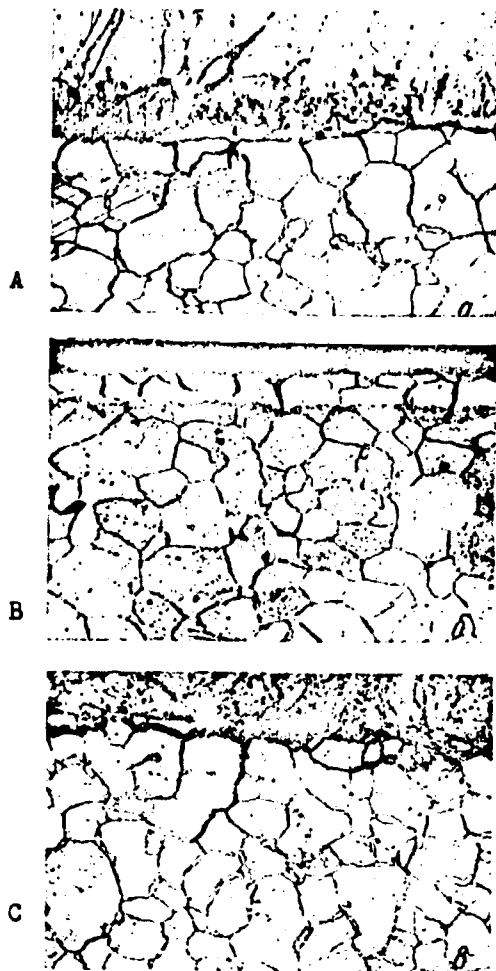


Figure 124. Microstructure of surface layer of specimens of armco iron after tests for long term strength in contact with zinc at 500° C (X 150):

a, second series of specimens,
 $\sigma = 3 \text{ kg/mm}^2$, $\tau = 364 \text{ hr}$;
 b, third series,
 $\sigma = 5 \text{ kg/mm}^2$, $\tau = 94 \text{ hr}$;
 c, fourth series,
 $\sigma = 4 \text{ kg/mm}^2$, $\tau = 598 \text{ hr}$.

Analysis of a microstructure of the iron-zinc boundary showed that the intermetallide film was not well bonded to a surface of the specimen*. The appearance of a new phase along the grain boundaries was noted in specimens subjected to the influence of zinc for extended periods of time. This phase is apparently an iron-zinc alloy with high zinc concentration, separated as the specimen cooled.

* The bands which can be seen on the photographs of the sections (see Figure 124) were formed as a result of oxidation during etching.

The changes in the processes of creep and long term strength are a result of the effects of the corrosion, adsorption and diffusion factors. The role of corrosion can be seen from a comparison of results of tests for long term strength in the pure and saturated zinc (Figure 121). Comparison of the long term tensile strength after 1000 hours indicates that the influence of pure zinc leads to a decrease in the strength relative to the initial value of 74%, whereas if the corrosion factor is eliminated the material undergoes a decrease in strength of 65%. The corrosion effect of zinc on armco iron is manifested in this case as general dissolution, particularly dissolution of inter-crystallite zones, which are in less favorable energetic conditions than the sectors of metal within crystallites.

The time dependence of strength (see Figure 121) and the dependence of creep rate on stress (Figure 123) indicate the influence of the adsorption factor in the deformation of iron in liquid zinc. Comparison of the results of testing of specimens in the third and fourth series indicates that the decrease in the surface energy of the deformed metal-medium boundary leads to a decrease of time to rupture and an increase in creep rate with identical stress value.

The diffusion influence of liquid zinc on armco iron is confirmed by the decrease in time rupture and the increase in creep rate of specimens in contact with solid iron-zinc alloy in comparison to specimens whose internal cavity was filled with argon (see Figure 121 and 123). The diffusion penetration of zinc into the wall of the specimens was determined directly by chemical spectral analysis. It was found that the zinc appears near the external surface of specimens tested over 100 hr. If we base the determination of the diffusion factor on the dependence $D \approx l^2/t$, where l is the distance, t is the time, the order of magnitude of the effective diffusion factor of zinc into iron is $1 \cdot 10^{-8} \text{ cm}^2/\text{sec}$. In the presence of zinc in the material of the specimens was confirmed by metalographic analysis (Figure 124).

The influence of the diffusion factor on creep and long term tensile strength of armco iron in zinc is also confirmed by the following experiment. Two specimens filled with zinc which had been saturated with iron were held in a furnace in the unloaded state at 500°C , one for 38 hours, the other for 200 hours. Their holding times corresponded to the time to rupture specimens in the fourth series tested at stresses of 7 and 5 kg/mm^2 respectively. Thus, the quantity of zinc which diffused into the material of the specimens was approximately identical (if we do not consider the influence of stresses and plastic deformation on diffusion). After this holding and removal of zinc from the

internal surfaces (melting of the liquid metal with subsequent etching in 20% NaOH) the specimens were tested for long term strength at stresses of 7 and 5 kg/mm². Although they underwent the influence of the diffusion factor along during the tests, as did the corresponding specimens of the fourth series, their time to rupture was found to be less -- 26 and 68 hours respectively.

This result can be explained by the fact that these specimens contained approximately the same quantity of zinc at the beginning of the test for long term strength as the corresponding specimens from the fourth series contained at the end of their testing. The stable creep rates on the specimens subjected to preliminary diffusion were $8.8 \cdot 10^{-2}$ and $2.8 \cdot 10^{-2}$ % / hr respectively. Comparing these figures with the data of Figure 123, we see that they are near the values of creep rate of specimens in the fourth series, the rate of the specimen tested at 5 kg/mm² stress being even somewhat higher which is also related to the specific feature of the test just noted.

Comparing the placement of the lines of long term strength and creep of armco iron on Figure 121 and 123, constructed using the results of tests of the fourth series of specimens, we reach the conclusion that the corrosion, adsorption and diffusion factors act simultaneously when armco iron is exposed to pure liquid zinc. Due to their simultaneity and identical direction, the effects of corrosion, adsorption and diffusion must be inter-related and must influence each other. This in turn means that the resulting effect is not simply the sum of the influences produced by superimposing the influence of the various factors, but rather the result of the interaction of the corrosion, adsorption and diffusion factors.

We must note the quantitatively identical nature of the influence of all three factors on the long term strength and creep of the material. However, the degree of influence of each factor differs. Obviously, the intensity of the manifestation of the influence of corrosion, adsorption and diffusion depends on the nature of the solid and liquid metals and the experimental conditions (temperature, deformation rate, quantity of liquid metal, etc.). Therefore, we must expect that under certain conditions the influence of the each of these factors will predominate, while under other conditions the influence of the same factor may even be absent.

Thus, the results of experiments presented above indicate the complex nature of the influence of a liquid metal medium on a deformable solid metal. They also indicate the necessity of the individual approach to each solid metal -- liquid metal system.

A. Adsorption Effect

1. Mechanism Of The Adsorption Effect

We can see from the data represented in the preceding four chapters that the regularities of deformation and rupture of metals in an aqueative liquid metal medium are usually the same as in an inactive medium. For example, the effects of various factors (temperature, grain size, etc.) when metals are tested in active and inactive media are similar. The influence of the liquid metal causes only a change in a magnitude of the strength and plasticity characteristics of the metal. Therefore, we must consider that the mechanisms of deformation and rupture of the solid metal in the liquid metal are the same as in the inert medium. This conclusion indicates the possibility of using the results of investigation of the rupture and the deformation of solid metals with no consideration of the influence of the external medium in our study of the mechanism in the influence of adsorption -- active liquid metals.

Many investigators have estimated the theoretical strength of an ideocrystalline lattice [315 - 319]. Regardless of the models used in calculation, it has been found that consideration of the forces of the interatomic interaction alone leads to a similar expression in all cases for the rupture stress

$$\sigma = \lambda \sqrt{\frac{E\gamma}{a}}, \quad (177)$$

where E is the normal elasticity modulus; γ is the specific free surface energy; a is the crystalline lattice constant;

λ is a coefficient near unity (differing in the works of different authors).

It is well known that the actual strength of metals is two, sometimes three orders of magnitude lower than the theoretical strength. The first attempt to explain this differential is made by Griffith [320]. He suggested that the lower strength of actual solids results from cracks. Griffith solved the problem of the rupture of a thin plate of an isotropic material containing a penetrating crack of elliptical form with the large half -- axis perpendicular to the direction of application of the external force. Calculation produced the following expression for the rupture stress:

$$\sigma_k = \mu \sqrt{\frac{E\gamma}{c}}, \quad (178)$$

where c is the length of the crack (large half axis of the ellipse); μ is a factor near unity.

Griffith's equation can be easily produced by an analysis of changes in the energies of the metal resulting from the development of a crack [321]. Before the formation of a crack, the density of elastic energy in the metal is $\varepsilon = \sigma^2/2E$. The appearance of a crack of length c results in removal of the elastic stress over an area of approximately c^2 , or correspondingly to a decrease in energy of $\sigma^2 c^2/2E$. Considering the fact that the expenditure of work involved in the formation of the new surface is $2\gamma c$, we can produce an equation for the total increment of energy in the form

$$\Delta E = 2\gamma c - \sigma^2 c^2/2E. \quad (179)$$

Differentiating ΔE with respect to c , we find that the maximum energy increment is produced if the equality $2\gamma - \sigma^2 c/E = 0$. This means that with stresses less than $\sqrt{2E\gamma/c}$, a crack of length c will close spontaneously, but that after the critical value $\sigma_k = \sqrt{2E\gamma/c}$ is reached it will grow spontaneously, that is the solid metal will be ruptured.

In later works [322-325, 361] the resistance of solids with cracks to rupture was calculated with a different statement of the problem. The solutions were produced in all cases in a form similar to Griffith's equation (178); the difference was only in the value of coefficient μ . Experimental tests of equation (178) indicated that it corresponded well to experimental data if the rupture of the metals was brittle. In the case of plastic rupture, however, the calculated value of resistance to rupture differed essentially from the observed experimental value. If we assume that in the development of a crack the work is expended not only in the process of increasing the surface, but also in plastic deformation at the ends of the crack, we can introduce the quantity p , which represents the main work expended in increasing the length of the crack* per unit area, thus converting equation (179) to

$$\Delta E = 2\gamma c + pc - \frac{\sigma^2 c^2}{2E}. \quad (180)$$

On the basis of equation (180), the resistance to rupture is

* A crack of unit width is analyzed.

$$\sigma_R = \mu_* \sqrt{\frac{E(\gamma + p/2)}{c}} \quad (181)$$

Experimental data indicate that in plastic rupture of the metal $\gamma + p/2 \approx 1 \cdot 10^6 \text{ erg/cm}^2$ [326], where as in brittle rupture $\gamma \approx 1 \cdot 10^3 \text{ erg/cm}^2$. The value of the free surface energy of a solid metal produced by calculation using formula (178) agrees with the values produced on the basis of other estimates [114].

It follows from equation (181) that plastic deformation is important in the rupture of metals. Since p is a variable quantity in an actual crystal, that is, it has different values during different stages of the development of a crack as a result of various obstacles on the path of crack propagation, the Griffith condition in form (181) will be fulfilled only during certain time intervals and, consequently, it determines the value of critical stress necessary for extension of a crack over a certain sector. Thus, the Griffith condition for brittle materials is correct for the specimen as a whole, while for plastic materials it is correct for individual sectors of the specimen. As a result of this, the rupture of brittle materials occurs when high propagation velocity of the crack -- almost instantaneously, while the crack propagates in plastic materials in jumps. During periods when the crack is stopped, when its dimensions are temporarily stable, plastic deformation occurs, after which condition (181) is fulfilled once more and the crack moves further. As a result, the mean rate of development of the crack c over the entire cross section of a plastic specimen is much lower than the speed of a crack in a brittle specimen.

One defect of Griffith's hypotheses is its analysis of a crack in a solid body as such, that is the supposition of the presence of the cracks of critical dimensions before the beginning of formation. Further investigations have shown that such cracks are absent in materials in the initial state and, consequently, the processes of their formation must be clarified. A. V. Stepanov [327-329] first indicated the decisive role of plastic deformation in the formation of seed cracks in solids. Later, this idea was extended to metals by N. N. Davidenkov [330]. The modern theory of dislocations essentially concretizes these concepts.

There are several dislocation models of the formation of cracks in metals (Figure 125). The best developed and most wide spread variant is that which explains the formation of seed cracks as a result of concentration of tensile stresses at the head of accumulation of boundary dislocations before an obstacle (Zener-Mott-Stroh model [331-334]; see Figure 125, a). In this case,

the crack is located at an angle of 70° to the slipping plane. Gillman and V. N. Rozhanskiy have demonstrated the possibility of formation of cracks in the slipping plane, in which accumulation of boundary dislocations occurs [335, 336] (see Figure 125, b). V. L. Indenbaum established the possibility of appearance of such a crack as a result of movement of dislocations in a curved crystalline lattice [337] (see Figure 125, c). A crack seed may also be formed due to rupture of a vertical wall of dislocations [338, 339] (see Figure 125, d). Cottrell established that a crack may arise upon interaction on accumulated dislocations moving in intersecting planes of slippage [340] (see Figure 125, e). Formation of a crack may occur as a result of imposition of tensile stresses from two dislocation accumulations of opposite sign located in two slipping planes which are parallel and located near each other (Fujita model [341]) (see Figure 125, f).

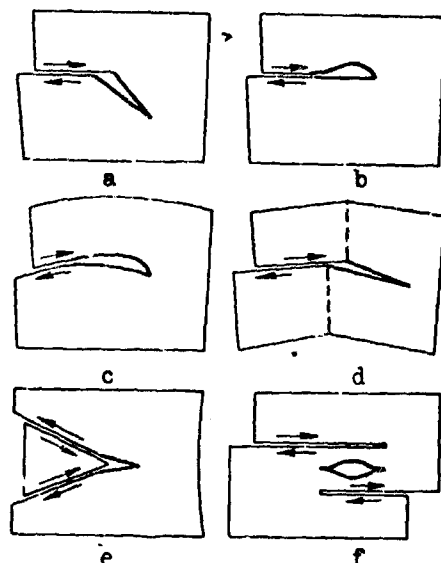


Figure 125. Diagrams of formation of internal cracks in metal [342].

Analysis of the conditions of development of a crack in a solid metal in contact with an adsorption active liquid metal melt was performed by Ye. D. Shchukin and V. I. Likhtman [344-345]. This analysis is applicable to practically any of the particular models of crack formation indicated above. The area of localization of an incomplete shear (not extending through the entire cross section of a crystal) with a length in the slipping plane of S is analyzed. Two stages are differentiated in the process of crack development. In the first stage, the shear stress τ_s , causing movement of dislocations and formation of deformation heterogeneities of the incomplete shear type, is decisive. As a result, local stress concentrations appear which

exceed the applied stress τ_s by many times. The sharp concentration of normal stresses arising leads to the appearance of equilibrium seed cracks (not extending to the entire crystal under the normal stresses). The dimensions of such a crack can be determined as follows.

The density of elastic energy ϵ near the area of the incomplete shear is proportional to $\tau_s^2 S / 2Er$, where E is the normal elasticity modulus; r is a distance from the point in question to a certain point in interval S , where $S \geq r > r_0$, where r_0 is the minimum distance for which the laws of the theory of elasticity are still applicable ($r_0 \approx 10^{-7}$ cm). As a result of formation of a crack of length c , elastic stresses are removed over the incomplete shear interval S and over a distance approximately equal to c to the side of area S . Considering the work expended in the formation of the surfaces of the crack, equal to $2\gamma c$, the total change in energy can be written in the form

$$\Delta E \approx 2\gamma c - \int \int e(r) dS \approx 2\gamma c - \frac{\tau_s^2 S^2}{E} \ln \frac{ac}{r_0}, \quad (182)$$

where a is a coefficient near unity. The magnitude of the equilibrium crack can be found from the condition $d(\Delta E)/dc = 0$:

$$c = \beta \frac{\tau_s^2 S^2}{E\gamma}, \quad (183)$$

where β is a dimensionless coefficient near unity.

A crack of maximal size is formed if the area of incomplete shear encompasses the entire cross section L of the monocrystal (or grain of polycrystalline metal):

$$c_{\max} = \beta \frac{\tau_s^2 L^2}{E\gamma}. \quad (184)$$

Thus, the dimensions of an equilibrium crack are determined by the value of free surface energy. It follows from equation (184) that in a surface active liquid metal, the length of the maximum equilibrium crack is greater than in an inert medium.

In the second stage of development of a crack, the decisive role is that of the normal stress σ . Rupture occurs when the critical value of normal stress σ_k is reached (for the most dangerous crack)

$$\sigma_k = \mu \sqrt{\frac{E\gamma}{\epsilon_{\max}}}. \quad (185)$$

We can see from equations (185) and (184) that in a surface active liquid metal, the value of resistance to rupture is less than in an inactive medium. These equations also indicate that disruption of monocrystalline specimens with various orientations relative to the applied tensile stress should occur with a definite relationship between normal and shear stresses, namely with constant value of their product

(186)

$$\sigma_n \tau_{nk} = K^2,$$

where $K = \propto \sqrt{E\gamma/L}$.

Representing the angle of the inclination of the plane of rupture to the direction of application of the force at rupture of the specimen χ_1 , we can produce the following formulas on the basis of (186) and known geometric relations for σ and τ_s [345]

$$\sigma_n = K \sqrt{\operatorname{tg} \chi_1}, \quad (187)$$

$$\tau_{nk} = K \sqrt{\operatorname{ctg} \chi_1}. \quad (188)$$

Chapter I presented experimental data on the rupture of pure zinc monocrystals at liquid nitrogen temperature and monocrystals with a thin surface film of liquid mercury at room temperature, which agreed well with equations (186-188). On the basis of these data, it has been calculated [190] that in the first case $K_{Zn} = 209 \text{ g/mm}^2$, while in the second case $K_{Zn-Hg} = 95 \text{ g/mm}^2$.

It follows from this that the reduction in strength of zinc monocrystals in mercury is caused by a decrease in surface inter-phase energy, which amounts to $\gamma_{Zn-Hg} / \gamma_{Zn} \approx (K_{Zn-Hg} / K_{Zn})^2 \approx 1/5$. Thus, if the free surface energy of zinc is approximately 1000 erg/cm^2 , the mercury coating reduces it to approximately 200 erg/cm^2 .

On the basis of the concepts concerning the mechanism of the influence of liquid metals on solid metals in the process of deformation presented above, we can explain many other effects observed experimentally in short-term mechanical tests as well (see Chapter I). The disappearance of the influence of the liquid metal medium as the temperature is increased was first explained in a work by V. N. Rozhanskiy, in the Pertsov et al. [195]. These concepts were then developed in [240, 346, 450]. The explanation was presented using an expression for the probability of penetration of an obstacle by an accumulation of dislocations located in a common plane presented by Stroh [347]:

$$W(T) = 1 - \exp\left(-\frac{\omega l t_0}{b} e^{-U/kT}\right), \quad (189)$$

where U is the activation energy used by the dislocations to cross the barrier on the path of development; ω is a natural frequency of thermal oscillations of the atoms; l is the length of the retarded dislocation front; t_0 is the time required for accumulation of dislocations sufficient to form a crack; b is the Burger vector. Structure of equation (189) defines the sharp change in probability of plastic deformation from 0 to 1 in a narrow temperature interval located on either side of a certain mean critical temperature

$$T_k = \frac{U}{k \ln \frac{\omega l t_0}{b}}. \quad (190)$$

On the basis of experimental data on tensile rupture of monocrystals of zinc, an estimate has been formed of the quantities included in formula (190), giving a value of about 1 eV for the activation energy. Then, the values of the variables were substituted in the formula (189) and it was used to construct the temperature dependence of the probability of plastic deformation of zinc monocrystals covered with mercury. It was found that the temperature interval of the change of $W(T)$ from 0 to 1 agrees fully with the interval of restoration of plasticity (relative elongation) of amalgamated monocrystals to the level of pure monocrystals, that is in both cases this interval was 120-160° C. Thus, the effect of restoration of plasticity as test temperature was increased for rupture at constant deformation rate results from an increase in probability of plastic deformation due to thermal fluctuations. Due to this, the concentration of stresses in the end portion of the crack is decreased (the stressed state is discharged as a result of plastic deformation) and an increase in stress becomes necessary for the crack to grow to the Griffith dimensions.

The nature of the solid and liquid metals and the test conditions result in the formation of three variants of the relationship of melting points of the base metal T_0 , liquid metal T_1 and critical brittleness temperature T_k [345]. With the relationship $T_1 < T_k < T_0$, a reduction in plasticity and strength of the base metal in the temperature interval T_1 - T_k is noted. Where $T_1 < T_0 \leq T_k$, the effect of the adsorption influence of the liquid metal is noted from the melting point of the medium right up to the melting point of the base metal. When $T_k < T_1$, the effect does not appear at all. The first of these

three variants is observed, for example, when zinc is tested in liquid mercury, the second - when carbon steels are tested in liquid tin (see Chapter I, Section 2).

Another effect - the influence of the liquid metal on the dependence of the strength of the polycrystalline metal on grain size (see Chapter I, Section 4) -- can be easily explained using the Stroh-Petch relationship [334, 348, 349]

$$\sigma_k = \sigma_0 + \left(\frac{6\pi G\gamma}{1-\nu} \right)^{1/2} d^{-1/2}, \quad (191)$$

where σ_k is the tearing resistance; G is the shear modulus; γ is the free surface energy; d is the grain diameter; ν is Poisson's coefficient; σ_0 is the material constant.

We can see from equation (191) that the slope of line $\sigma_k - d^{-1/2}$ in relation to the abscissa ($d^{-1/2}$) decreases with decreasing surface energy of the solid metal. This result was also produced in experiments with adsorption active liquid metals (see Chapter I, Section 4). Using dependence (191) and experimental data on tensile rupture on 70/30 brass, the authors of [226] showed that the surface energy of brass in contact with liquid mercury is 280 erg/cm², whereas in an atmosphere of its own vapors it is 1500 erg/cm². Obviously, a dependence such as (191) should also be retained for the strength limit, which is confirmed by the experimental data (see Figure 83).

The linear dependence between T_k and $\ln d$, established in [231] in tests involving the rupture of specimens of 70/30 brass covered liquid mercury, has been confirmed by theoretical analysis of brittle ruptures performed by Fetch [350]. The formula which he presents:

$$T_k = A + \frac{1}{2} \ln d$$

indicates that the value of A depends on the value of surface energy of the metal deformed. The absence of any results of tests involving the termination of $T_k = f(d)$ for the same material in a surface active liquid metal and an inert medium prevents a check of the dependence of $A = A(\gamma)$ produced in [350].

Chapter I (Section 1, 6 and 7) shows the increase in the degree of action of liquid metals with increasing initial strength of the solid metal on the basis of experimental data. This effect can be explained by the adsorption influence of the medium, if we consider that the increase in strength corresponds to an increase in barriers across the path of movement of

dislocation accumulations. Then when an influence of the medium is present, the formation of cracks in a material with high initial strength occurs with lower applied stress than in a metal with lower strength. Obviously, the size of the barriers created by various types of hardening is not identical. For example, dispersion hardening of an alloy creates more serious obstacles to the movement of dislocations than work hardening. Correspondingly, the effect of the action of liquid metal on a dispersion-hardened alloy is greater than on a work hardened alloy. The increase in the barriers resulting from the appearance of additional defects in the crystalline lattice is also explained by a reinforcement of the influence of the surface active liquid metal medium on the metal after irradiation (see Chapter I, Section 9).

In correspondence with the concepts which we have presented, the formation of seed cracks is assumed to occur within the metal being deformed (mono- or polycrystalline). In the opinion of the authors of reference [344-345], the liquid metal penetrates into these cracks by two-dimensional migration along the hollowed dislocation nuclei which may be formed in the very early stages of deformation. In the presence of internal cracks in the mono-crystalline specimens has been established by microscopic investigation. However, this nature of the development of cracks under the influence of the liquid metal is apparently relatively rare. Even in inert medium, particularly at high temperatures, the cracks are usually formed on the surface of the metal and then gradually extend into the entire cross section. The formation of surface cracks in polycrystalline metals has been confirmed, for example, in a work by S. T. Kishkin and A. A. Klypin [351] by grinding off the surface layers, and also in [352] by periodic loading of a specimen with compressive stresses, with constantly applied tensile stresses. Due to oxidation of the surface cracks, the loading with compressive stresses caused no increase in long term strength of the materials.

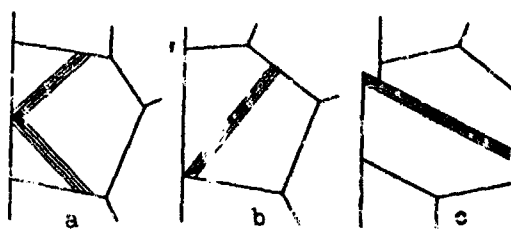


Figure 126. Diagrams of formation of surface cracks.

The electron microscope method was used to establish the formation of cracks on the surfaces of specimens of nickel in the very earliest stage of extension at constant rate [353] .

Surface cracks were observed in the deformation of monocrystalline specimens in a liquid metal medium, which can be seen easily on photographs presented in [7, 354] . Naturally, when cracks form on the surface the question of penetration of the liquid metal medium into the crack by the mechanism mentioned above is answered.

The mechanisms of formation of surface cracks may be as follows. Parker [355] considers it possible that cracks may be formed at points where two intersecting slipping planes reach the surface (Figure 126, a). Rostoker, et al [8] believe that surface cracks may arise upon formation of accumulation of dislocations before the grain boundary near the surface of the metal (see Figure 126, b). Of these models, the former, as we can see from Figure 126, a, may operate in both monocrystals and polycrystals. The formation of a surface crack is also possible at the point where a slipping plane reaches the surface of the specimen (mono- or polycrystalline). We know that plastic deformation causes steps to form here (see Figure 126, c) with dimensions of up to 1000 Å [356, 354] . Assuming that the relationship $\sigma_m \approx \sigma \sqrt{l/r}$ exists between the applied stress σ and the maximum stress at the point of concentration σ_m , and considering that $r = 3.5 \cdot 10^{-8}$ cm, while $l \approx 10^{-5}$ cm, we find $\sigma_m \approx 17\sigma$. Consequently, with relatively low applied stresses, rupture of the interatomic bonds may occur at the point where dislocations reach the surface, resulting in formation of cracks. The growth mechanism of seed cracks already present on the surface of the crystal, formed due to interaction with boundary dislocations passing nearby, was suggested by Orovan [357] .

We must point out that the analysis of the adsorption influence of a liquid metal on a solid metal performed above is insufficient, since it gives us no picture of rupture at the "atomic level." In recent times, investigations have developed in the area of analysis of atomic interactions [227, 446-448] . Further development of the theory of adsorption effects during rupture will doubtless occur in the direction of consideration of the active interaction of atoms of liquid and solid metals at the end of a crack. An attempt has already been made on the basis of analysis of this interaction to conclude an equation for the long term strength of a solid metal in an adsorption active liquid metal medium [358, 359] .

In recent times, we have come to believe that the edges of cracks formed as metal ruptures are not rounded, but are formed of two asymptotically approaching the crystallographic planes right down to the normal distance between them, corresponding to a crystalline lattice constant [360-363]. However, it can be easily shown that such a crack cannot be equilibrium and should cause rupture of the solid body in a field of tensile forces. Actually, the distance between atoms in the terminal area of the crack is increased gradually and regularly, a pair of atoms should be found, the strength of interaction between which will be equal to the theoretical strength so that, consequently, the bond between them should be broken. Then, the next pair of atoms will be in a similar situation, etc, as a result of which complete separation of the crystal into two parts will occur. This conclusion agrees with the results of calculations of A. N. Orlov [364] and Yu. M. Plishkin [365], who demonstrated the impossibility of the existence of equilibrium cracks in a crystal with an ideal lattice.

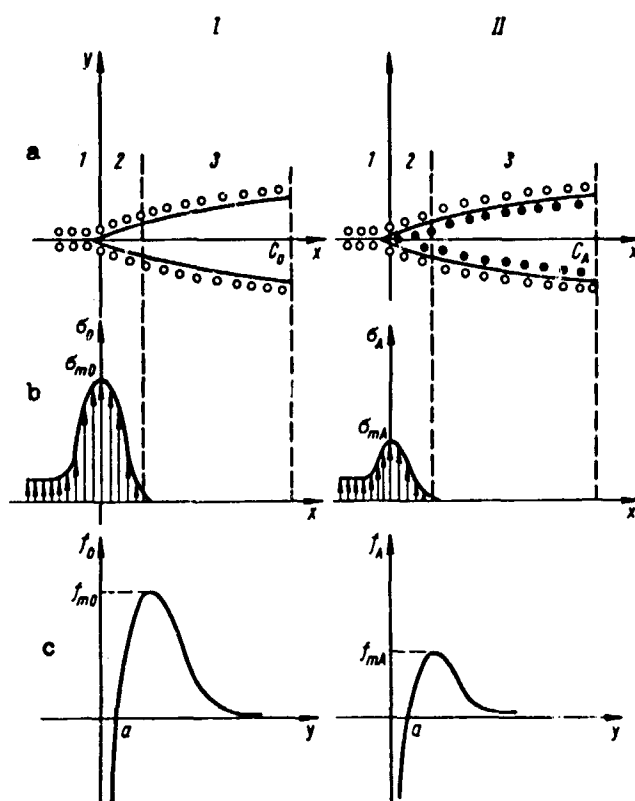


Figure 127. Diagram of crack (a), distribution of normal stresses at crack edge (b), and changes in force of interaction of two atoms with changing distances between them (c); I, inert medium; II, adsorption active medium.

Thus, in the end area of an equilibrium crack, the approach of a plane cannot be even everywhere: in the area of maximum values of atomic interaction force, relatively sharp approach of the planes should be observed (Figure 127). The change in crack form may be related to plastic deformation of the metal. We will differentiate three areas in such a crack [361]: 1, the area where stresses increase from their nominal value to their maximal value; 2, the area where normal stresses change from the maximal value to zero*; 3, the internal area of the crack, where the forces of the interaction between atoms on opposite surfaces are practically equal to zero. This distribution of stresses (see Figure 127, b) is determined by the well known nature of the dependence of forces of interaction between two atoms on changes in the distance between them (see Figure 127, c).

In correspondence with the above, the configuration of an equilibrium crack is such that the value of maximal normal stress at the boundary of the first and second areas σ_{m0} should be less than the theoretical strength σ_T , that is, σ_{m0} less than σ_T . The value of σ_{m0} depends on the value of the nominal stress σ , and this dependence is determined [366] by the relationship

$$\sigma_{m0} = \sigma \sqrt{\frac{c_0}{r_0}}, \quad (192)$$

where c_0 is the depth of the crack, equal to the distance from the external surface of the solid to the boundary of areas 1 and 2; r_0 is the radius of curvature of the crack of this boundary. The development of a crack should begin at the moment when conditions $\sigma_{m0} = \sigma_T$ is fulfilled. This moment can be determined as the loss of stability by the crack.

If a solid metal is located in a surface active liquid metal, the atoms of the liquid metal will penetrate into the crack and interact with the atoms of the solid metal located on the surfaces of the crack in the second and third areas. (See Figure 127, II a). This results in a decrease in normal stresses in the end areas of the crack (See figure 127, II b), which results in a decrease in forces of interaction between atoms of the solid metal (see Figure 127, II c) due to changes in their energy field due to the influence of the atoms of the liquid metal.

* A boundary between the second and third areas is largely arbitrary.

Since $f_{mA} < f_{mO}$, the critical stress in the end area in the presence of a surface active medium will be achieved with lower nominal stress than in the inert medium. The result of this is rupture of the solid metal in the liquid metal medium at decreased strength value.

However, it must be noted that a crack, after reaching its critical state, can move only over a slight distance if defects in the structure of the crystal of lattice (grain boundaries, packing defects, accumulations of dislocations, etc.) are encountered in its path, causing a decrease in maximum stress in the end area below the value of theoretical strength. This results in temporary stabilization of the crack, and further propagation can occur only with an increased nominal stress.

Under the conditions used in long term strength testing, movement of the crack becomes possible if thermal fluctuation arises in the end area, causing σ_{mA} to reach the value σ_c . Let us represent α the width of the end area of the crack where the stress exceeds the nominal value. Keeping in mind that for a non-equilibrium crack

$$\int_0^\alpha \sigma_A dx = 2\gamma_A, \quad (193)$$

where γ_A is the surface energy of the division boundary of the solid and liquid metals, and expressing this integral approximately for an equilibrium crack in the form of the product $\frac{1}{2} \alpha \sqrt{\frac{c_A}{r_A}}$

we see that the value of thermal fluctuation required to convert the crack* from the equilibrium state to the nonequilibrium state with fixed constant nominal stress σ is approximately

$$\left(2\gamma_A - \frac{1}{2} \sigma \alpha \sqrt{\frac{c_A}{r_A}}\right) a^2, \text{ where } a \text{ is the crystalline lattice constant.}$$

However, this expression does not take full consideration of the work expended in the development of the crack. To do this, we must also add the quantity Q , representing the work expended in plastic deformation and the energy dissipated in the form of heat. Considering this, we can write the following formula for the probability of rupture of bonds in the end portion of the crack:

$$W = \omega e^{-\frac{Q + 2a^2\gamma_A - \frac{1}{2}\sigma\alpha^2\sqrt{\frac{c_A}{r_A}}}{kT}}, \quad (194)$$

* Calculation performed for a crack in a monoatomic layer.

where ω is the characteristic frequency; k is Boltzman's constant; T is the absolute temperature. Using formula (194), for the rate of the development of the crack under long term strength testing conditions, we produce the equation

$$\frac{dc_A}{dt} = \omega a e^{-\frac{Q+2a^2\gamma_A - \frac{1}{2}\alpha a^2\sigma \sqrt{\frac{c_A}{r_A}}}{kT}} \quad (195)$$

Obviously, the configuration of the end portion of a crack depends on the nominal stress. As a result of the interaction of atoms of the surface active liquid metal with atoms of the solid metal, the configuration of the crack also depends on γ_A . Thus, the radius of the end portion of the crack is a function of the nominal stress and the surface tension. As a first approximation we will consider that this function has the form

$$r_A = \frac{\beta}{\sigma^m \gamma_A}, \quad (196)$$

where β and m are constant coefficients. Substituting (196) into (195), we produce

$$\frac{dc_A}{dt} = \omega a e^{-\frac{Q+2a^2\gamma_A - \frac{1}{2}\alpha a^2\beta^{-1/2}\sigma^{1+m\gamma_A/2} \sqrt{c_A}}{kT}} \quad (197)$$

Using this last formula, we can write an equation for determination of the time to rupture of the metal

$$\tau = \frac{1}{\omega a} e^{\frac{Q+2a^2\gamma_A}{kT}} \int_0^{c_{Akp}} e^{-\frac{\alpha a^2\sigma^{1+m\gamma_A/2}}{2\beta^{1/2}kT} \sqrt{c_A}} dc_A, \quad (198)$$

where c_{Akp} is the critical (Griffith) crack length, beginning with which its rate of propagation becomes near the speed of sound.

Introducing the following substitution to equation (198)

$$x = \frac{\alpha a^2\sigma^{1+m\gamma_A/2}}{2\beta^{1/2}kT} \sqrt{c_A}, \quad (199)$$

we produce

$$\tau = \frac{8\beta}{\omega a^5} \left(\frac{kT}{\alpha}\right)^{3/2} e^{\frac{Q+2a^2\gamma_A}{kT}} \sigma^{-m\gamma_A-2} \int_0^{x_{kp}} e^{-x} x dx. \quad (200)$$

The integral in equation (200) is practically equal to unity, since the upper limited integration x_{kp} is on the order of $10^3 - 10^4$. Therefore, we can replace the integral with coefficient λ , approximately equal to unity, but having dimensionality.

Finally, the equation for time to rupture of the metal under long term strength testing conditions takes on the form

$$\tau = \frac{8\pi\gamma_A}{\omega_0^2} \left(\frac{T}{\alpha} \right)^2 e^{\frac{Q+2\alpha\gamma_A}{kT}} \sigma^{-n\gamma_A-2}. \quad (201)$$

Analysis of equation (201) leads to the conclusion that it reflects properly the dependence of time to rupture on stress and temperature. In the first case this dependence is exponential, that is, as has been confirmed by many experimental data involving long term testing of structural materials *. The dependence of time to rupture on temperature both on the basis of (201) and on the basis of experimental data, is exponential (with an accuracy to the factor before the exponent, practically constant throughout the entire range of temperatures for which experimental results are generally presented).

Evaluating equation (201) from the standpoint of its reflection of the dependence of time to rupture on the value of surface interphase energy, we can see that it reflects this dependence properly. Thus, it follows from (201) that in a surface active liquid medium, the time to rupture of the material should be decreased in comparison with an inactive medium with identical stress and temperature in both medium. It also follows from (201) that this slope of the long term strength line in relation to the time access (in coordinates $\log \sigma - \log \tau$) constructed according to the results of tests in a surface active liquid metal is steeper than the line for tests in an inert medium. Furthermore, equation (201) shows that the activation energy for rupture, solid metal in contact with a liquid metal is lower than the activation energy for rupture in an inert medium.

These regularities agree fully with the results of tests for long term strength of copper in liquid bismuth (see Chapter II) and alloy EI437B in liquid sodium (see Chapter V, Section A2), that is when the action of the liquid metal medium was by adsorption.

We can make an estimate of the magnitude of the change in surface energy of copper when tested for long term strength in liquid bismuth using the boundary of activation energy for rupture presented in Chapter II, Section 2. On the basis of equation (201) we can produce

* As was already indicated in Chapter II, with brief test durations and exponential dependence is generally observed [252-254].

$$\gamma_T - \gamma_{T,\ell} = \frac{k}{R} \cdot \frac{Q_T - Q_{T,\ell}}{2a^2}, \quad (202)$$

where γ_T and $\gamma_{T,\ell}$ represent the specific free surface energy of the boundary of the solid metal with the inert medium and with the surface active liquid metal respectively; Q_T and $Q_{T,\ell}$ represent the energy of activation of rupture in the inert medium and in the surface active liquid metal.

It was shown in Chapter II, Section 2, that when copper was tested for long term strength in air, $Q_T = 38.6 \text{ kcal/g} \cdot \text{atom}$, while in liquid bismuth $Q_{T,\ell} = 23.4 \text{ kcal/g} \cdot \text{atom}$. Calculations using formula (202) will be performed assuming $a = 3.5 \cdot 10^{-8} \text{ cm}$. Substituting these values into (202), we find that the decrease in surface energy of copper is the result of the action of the bismuth was 430 erg/cm^2 . It has been experimentally established [367, 368] that $\gamma_T = 1270 - 1680 \text{ erg/cm}^2$, $\gamma_{T,\ell} = 280 \text{ erg/cm}^2$, that is, $\gamma_T - \gamma_{T,\ell} = 990 - 1400 \text{ erg/cm}^2$. Consequently, calculations using (201) - (202) yields a value of change in surface energy which corresponds in its order of magnitude to the experimentally determined value, which is good agreement.

In all probability, the value of the difference $\gamma_T - \gamma_{T,\ell}$ determined from the data on long term strength should always be less than that determined directly, since in the first case during some time intervals in the development of the crack the liquid metal will not succeed in filling its end area, while during the second case experiments are performed in equilibrium conditions. Thus, the value of the change in surface energy calculated according to long term strength data is an effective value rather than a true value. We note also that the exponential dependence of time to rupture on the inverse temperature produced for copper (see Chapter II, Section 2) may not be observed over the broad range of temperatures as a result of the changes in surface tension as temperature changes [369].

We have analyzed the influence of an adsorption active liquid metal on the process of rupture during short-term testing of materials under tensile stress at constant rate and during long term strength testing. The experimental data presented in Chapter IV indicate the adsorption influence of the liquid metal medium on the process of rupture under fatigue testing conditions as well. As we know [370, 371], fatigue rupture is a result of performance of repeated microplastic deformations in the metal. At a certain

stage in their development, the formation of a fatigue crack becomes possible. The formation of this crack may occur as a result of the action of the mechanisms mentioned earlier [370], or as a result of a mechanism which is specific for testing under variable load, such as extrusion or intrusion [372-374].

An adsorption active liquid metal influences the formation of fatigue cracks, since they generally arise on the surface of the deformed specimen. However, this influence is most strongly felt in the stage of development of a crack, since according to [370], this stage makes up 90-97% of the time to rupture of a specimen. At the present time, this stage has been insufficiently studied even for metals which are not subjected to the influence of a corrosive medium. However, doubtless processes of microplastic deformation are important in this stage, preparing the metal at the end portion of the crack for rupture of the interatomic bonds. It is quite natural that rupture of bonds and the corresponding jump in the crack into the next sector of the metal, not as yet prepared for the rupture, occur in the adsorption active liquid metal as a result of interaction of atoms of the medium and the metal being deformed in the end portion of the crack at lower nominal stress or after a shorter preparatory period than in an inactive medium with identical stress amplitude. Obviously, the general regularities of the adsorption action of the liquid metal, noted earlier for other conditions of deformation of the metal are correct for fatigue tests as well.

Up to this point, they have analyzed the influence of a surface active liquid metal on the development of rupture cracks in a solid metal. This influence results in a deep decrease in total plasticity of a strength and time to rupture of deformed metal. Another group of effects of the action of a liquid metal medium is related to the facilitation of plastic deformation. The facilitation of deformation results from a decrease in the yield point and hardening factor during extension at constant rate, as well as an increase in the creep rate when the metal being deformed is in contact with a low-melting liquid metal (see Chapters I and III).

These effects, as Ye. D. Shchukin first showed [375], are determined by a decrease in the energy barrier preventing movement of dislocations to the surface of the metal. The existence of this barrier is related to the formation of steps of a new surface at the point where the boundary dislocations reach the surface. The width of this step is equal to component b in the Burger vector normal to the contour of the slipping plane and located in

it. Therefore, the maximum value of the surface energy barrier* is $U_m = ab\gamma$ or $U_m = b^2\gamma$, if $a = b$. The presence of the energy barrier in turn leads to the necessity of increasing the shear stress acting in the plane in order to complete the shear movement.

Let us estimate the excess value of shear stress resulting from the surface barrier. The work expended on displacement of the boundary dislocation of unit length over a distance equal to the crystalline lattice constant is expressed [376] by the equation

$$A = b^2\tau_s, \quad (203)$$

where τ_s is the shear stress acting in the plane of movement over dislocation. The magnitude of work calculated per atom (or over a sector of the dislocation line of length b) is

$$A = b^3\tau_s. \quad (204)$$

When the dislocation reaches the surface of the metal, additional work $b^2\gamma$ must be performed. Consequently, the work required to bring the dislocation to the surface (beginning calculation at distance b from the surface) is

$$A_n \approx b^2(b\tau_s + \gamma). \quad (205)$$

The additional work resulting from the necessity of overcoming the surface energy barrier can be performed by increasing the stress, which should have the magnitude

$$\tau_{s*} = \frac{A_n}{b^3}. \quad (206)$$

Using (205), we produce the following expression for the shear stress required for the boundary dislocation to reach the surface:

$$\tau_{s*} \approx \tau_s + \frac{\gamma}{b}. \quad (207)$$

Thus, when the stress is increased to a value equalling γ/b , the dislocation can overcome the surface energy barrier. Assuming $\gamma = 1000 \text{ erg/cm}^2$ and $b = 3.5 \cdot 10^{-8} \text{ cm}$, we find that $\tau_{s*} - \tau_s = 290 \text{ kg/mm}^2$. We can see from this that the surface barrier is a rather serious obstacle to the movement of dislocations.

Here we do not consider the force of the "mirror reflection," facilitating movement dislocations to the surface of the metal. This is possible due to a great steepness of the surface energy barrier [375].

It follows from formula (207) that as a result of the action of a surface active medium, leading to the decrease in surface energy of the solid metal from γ_T to $\gamma_{T.l}$, the excess value of shear stress is decreased by the quantity

$$\Delta\tau_s \approx \frac{1}{b}(\gamma_T - \gamma_{T.l}). \quad (208)$$

Thus, under the influence of a surface active liquid metal, completion of shear in the slipping plane in question, with formation of a surface step, occurs with a shear stress which is $\Delta\tau_s$ less than that required with the formation in an inert medium. We can see from formula (208) that the decrease in shear stress is proportional to the decrease in surface energy. Consequently, the effect of facilitation of plastic deformation is greater, the higher the surface activity of the liquid metal.

Analysis of the effect of facilitation of plastic deformation from the standpoint of the atomic interaction shows that it results from weakening of the forces of interaction of neighboring atoms in the external surface layer of the solid metal as a result of establishment of new bonds with atoms of the liquid metal. Weakening of the bonds facilitates their rupture as dislocations surface at lower stresses than when the influence of the medium is absent.

The diagram on Figure 128, which was suggested for explanation of the influence of surface active media on metal being deformed by Benedict [377] and M. I. Chayevskiy [378], gives a clear idea of this type of interaction. We can see from this diagram that the excess bonds of surface atoms of the solid metal, causing its free surface energy, are partially used in the interaction with atoms of the liquid metal, leading to a decrease in surface energy.

The importance of the surface in the process of deformation of a crystal is determined by the presence of the subsurface sources of dislocation, which have one point of attachment, as well as the increased density of dislocations sources in the surface layer [343, 344, 379]. For example, we know that the critical stress determining the activity of the Frank-Reed source with one attachment point is only half the critical stress of a source with two attachment points [376, 380]. The increased density of dislocation sources in the surface layer of metal has been established in experiments involving the etching away of this layer [379].

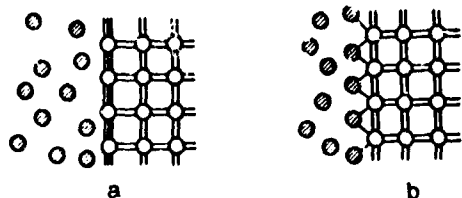


Figure 128. Diagram of interaction of atoms of liquid and solid metals at interphase boundary:

a, inert medium;
b, surface active medium.

Let us analyze the influence of a surface active liquid metal on the process of stable creep of a solid metal. Let us trace the movement of a boundary dislocation to the surface of the crystal, terminating in the formation of a step. First of all, the dislocation must travel from its initial point to the surface. We represent by t_d the time required for it to move to the surface, by Q_d the activation energy defining the movement of the dislocation over the sector. The probability of passage of a dislocation along a path within the crystal is $W_d = 1/t_d$ over:

$$W_d = \omega e^{-Q_d/RT}, \quad (209)$$

where ω is the natural frequency of thermal oscillations of the atoms. The final stage-movement of the dislocation to the surface - occupies a time equal to t_B , while the probability of movement to the surface $W_B = 1/t_B$ is defined by the value of the surface energy barrier, which is $\gamma - Q'(\sigma)/a^2$, where γ is the free surface; $Q'(\sigma)$ is the work performed by external forces; a is the crystalline lattice constants. From this the probability of movement of a dislocation to the surface is determined by the equation

$$W_s = \omega e^{-\frac{Q_d + a^2\gamma - Q(\sigma)}{RT}}, \quad (210)$$

where $Q(\sigma) = a^2 Q'(\sigma)$. The time required for performance of the entire process is $t_d + t_B$, while the probability $W = 1/(t_d + t_B)$ or

$$W = \frac{W_d W_s}{W_d + W_s}. \quad (211)$$

Since the creep rate v is proportional to the probability of plastic deformation,

$$v \sim \frac{e^{-\frac{Q_d + a^2\gamma - Q(\sigma)}{RT}}}{e^{-\frac{Q_d}{RT}} + e^{-\frac{a^2\gamma - Q(\sigma)}{RT}}}. \quad (212)$$

Let us analyze the two extreme cases. In the first case, the probability of overcoming barriers within the crystal is much less than the probability of overcoming the surface barrier, that is $W_d \ll W_B$. This relationship is apparently realized at high temperatures, when movement of dislocations is achieved by the mechanism of creeping over into neighboring slipping planes [381-383] and is determined by the activation energy for self-diffusion ΔG_d in equations (209) and (212) is in this case the self-diffusion activation energy⁷. Representing the creep rate at a certain stress level in the metal in an inert medium as v_T , and in a surface active liquid metal medium at the same stress as v_L , we can use relationships (211) and (212) to find $v_L/v_T \approx 1$, that is in this case the liquid metal will not influence the stable creep rate.

In the second case, we assume that the surface barriers are a more serious obstacle for dislocations than the internal barriers, from which it follows that W_B less than W_d . This variant is apparently possible at relatively low temperature with low applied stresses. One favorable condition for the appearance of this variant is low transverse size of the specimen. Using relationships (211) and (212) and assuming that the proportionality factor is (212) for v_L and v_T is identical, we produce*

$$\frac{v_L}{v_T} \approx e^{\frac{a^2(\gamma_T - \gamma_{T,L})}{kT}}. \quad (213)$$

Thus, in the second case the liquid metal can perform its adsorption effect. It follows from equation (213) that with identical applied stress and identical temperature, the rate of creep in the liquid metal is higher than in the inert medium ($\gamma_T > \gamma_{T,L}$ according to the condition). Equation (213) also shows that the influence of the liquid metal on the creep rate of the solid metal should decrease with increasing temperature.

This relationship of rates of stable creep in liquid metal and in an inert medium was observed in experiments with copper, the results of which are presented in Chapter III. Apparently in this case the value of the surface energy barrier is comparable to the value of the internal barriers.

* We note that an equation similar to (213) was produced earlier by V. I. Likhtman on the basis of the conception of creep as a process of viscous flow.

On the basis of formula (213), we produce the following approximate relationship:

$$\gamma_r - \gamma_{r,\ell} \approx \frac{k}{R} \cdot \frac{Q_r' - Q_{r,\ell}', \ell}{a^2}, \quad (214)$$

where Q_r' and $Q_{r,\ell}', \ell$ are the activation energies for stable creep in an inert medium and in liquid metal respectively. Comparing (214) and (202), we find

$$\frac{Q_r - Q_{r,\ell}}{Q_r' - Q_{r,\ell}', \ell} \approx 2. \quad (215)$$

Consequently, in the second variant the change of creep activation energy under the influence of surface active liquid metal is approximately half as great as the change of rupture activation energy.

This result follows from the fact that two atoms move into new positions as the crack length is increased by one interatomic distance, while when the dislocation reaches the surface of the crystal, only one atom moves into a new position. In other words, this result is caused by the formation of a new surface unit of area $2a^2$ upon the rupture of one atomic bond in the crack and a surface unit of area a^2 upon the rupture of one atomic bond, accompanied by appearance of a dislocation on the surface. This relationship thus demonstrates that the influence of the adsorption active medium on the process of rupture is greater than its influence on the process of deformation. The quantities characterizing the process of rupture of the metal should undergo greater change due to the adsorption influence of the medium in the quantities characterizing the process of deformation.

Let us use the experimental data on the temperature dependence on the creep rate of copper presented in Chapter III, Section 2. The experiments showed that the activation energy of stable creep of copper with a stress of 4kg/mm^2 in an inert medium is $Q_r' = 42.5 \text{ kcal/g.atom}$, while in liquid bismuth

$Q_{r,\ell}', \ell = 34.5 \text{ kcal/g.atom}$. Using the value $Q_r = 38.6 \text{ kcal/g.atom}$ and the value $Q_{r,\ell} = 23.4 \text{ kcal/g.atom}$ presented earlier, we find $(Q_r - Q_{r,\ell}) / (Q_r' - Q_{r,\ell}', \ell) = 1.9$. Thus, fulfillment of relationship (215), as well as the data presented above, indicates that the experiments with copper represent the second variant.

Another result follows from formula (213), which is correct for the second variant. Apparently, the increase in the stable creep rate under the influence of the liquid metal occurs in the following inequality is observed:

$$\gamma_r - \gamma_{r.l} > \frac{kT}{a^2}. \quad (216)$$

This inequality can be looked upon as the energy condition for the adsorption influence of the medium on the stable creep rate of the metal.

For the case of tests of copper for creep in liquid bismuth at temperatures of 300-400° C on the basis of equation (216), we find that $\Delta\gamma$ 80-100 erg/cm². Consequently, the increase in the creep rate of copper in liquid bismuth may occur if the decrease in free surface energy of copper in the liquid metal is about 100 erg/cm². Comparing this quantity with the values of $\Delta\gamma$, presented above, which were produced experimentally and by calculation using the results of creep tests, we find that they are in good agreement.

It was assumed earlier that the liquid metal influences the processes of deformation and rupture of the solid metal because it causes a decrease in free surface energy of solid metal. However, the fulfillment of this condition is necessary but insufficient for the observation of adsorption effects. Cases are possible when the liquid metal causes a strong decrease in surface energy but still the changes in strength and plasticity characteristics do not occur. These cases can be explained by considering the kinetic factor [384].

If the rate of propagation of a crack under the influence of an applied stress is higher than the rate of penetration of the liquid metal into the end portion of the crack, the influence of the medium on the strength and plasticity of the deformed metal will not be observed. Although in this case the interface energy of the newly formed surface is less than in the case of rupture in an inert medium, this decrease occurs after its formation.

Obviously, with sufficiently high rate of appearance of dislocations on the surface, the atoms of the liquid metal located at the point of appearance will be "repelled" in the direction of movement of the dislocation as a result of interaction with the atoms of the solid metal located in the slipping plane, which makes up the surface of the step. As a result, the next atom (looking at a one-dimensional model) must overcome the surface barrier of the same magnitude as in an inert medium. Thus, an increase in the rate of deformation should lead to disappearance of adsorption effects. This influence of deformation rates on strength and plasticity of a material in such a medium has been observed experimentally, for example during dynamic bending of steel discs covered with solder (see Chapter I, Section 3).

An approximate expression of the kinetic condition of adsorption reduction in strength can be produced for the case of deformation of the metal with constant rate [384]. We represent by δ the relative elongation of a specimen at the moment of rupture when tested at constant extension rate at $\dot{\epsilon} = d\epsilon/dt$ in an inert medium. The time to rupture of such a specimen is $t_0 = \delta/\dot{\epsilon}$. We represent further by v_1 the mean rate of penetration of liquid metal atoms into the end portion of a crack. Assuming that the diameter of the specimen is L , we find that the time required for extension of the liquid metal through the entire cross section is $t_1 \approx L/v_1$. Since the rate of movement of the liquid metal must be higher than the rate of propagation of a crack, the kinetic condition for the adsorption effect is written in the form $t_1 < t_0$

or

$$\dot{\epsilon} < \frac{v_1 \delta}{L}. \quad (217)$$

Thus, the rate of deformation of a specimen should not exceed $v_1 \delta/L$ if the adsorption decrease in strength is to occur*. However, condition (217) is quite approximate. The deformation of metal and development of cracks in it occur unevenly both in time and in space. Frequently, several cracks are formed in a metal each of which develops at a different rate at the same time. During the course of deformation to rupture of a specimen, each crack develops unevenly - its rate of propagation increases, then decreases. Dislocations move to various portions of the surface at different rates during deformation of metal as well. Their mean rate of movement, and consequently, the mean rate of appearance on the surface change with time as the stress state and structure of the metal change. Therefore, a surface active medium will fail to influence the development of certain groups of cracks and will fail to facilitate the appearance of certain dislocations on the surface in the various time intervals. During the same time interval, however, another group of cracks and dislocations might experience the full influence of the liquid metal. Finally, yet a third group may experience a partial influence. The effects of the liquid metal, evaluated according to the loss of strength, plasticity or decrease in time to rupture of the specimen, is an integral effect in relation to the elementary events of interaction of atoms of a solid and liquid metals. Nonfulfillment of the kinetic condition of the adsorption influence of the medium on the microscopic scale should lead to a decrease in the macroscopic effect relative to its maximal possible value. Consequently, the value of free surface energy in equations describing the rupture

* The more complex case when the quantity of liquid metal is limited and the liquid metal is dissolved in the metal of the specimen is analyzed in reference [384-387].

and the deformation of a solid metal in a liquid metal is an effective quantity, not a true (equilibrium) value.

I. describing the rupture of polycrystalline metals in a liquid metal medium (see Chapter I-IV) it was noted that cracks develop preferentially along grain boundaries. Although the particular role of grain boundaries may be related to intercrystalline corrosion and boundary diffusion of liquid metal atoms, the intercrystallite rupture under stress may also result from the adsorption influence of the medium methods [107, 215, 388].

As before, we will represent the free surface energy of the solid metal in an inert medium as γ_T , and in the liquid as $\gamma_{T,l}$; we will further suppose that the free energy of the grain boundaries of the solid metal is $\gamma_{T,T}$. Then we produce the value of $2\gamma_T$ for the work expended in the formation of a rupture surface of unit area in an inert medium if the crack is a transcrystallite type, or $2\gamma_T - \gamma_{T,T}$ if the crack is an intercrystallite type. The work expended in the formation of the same surface in case of rupture in a surface active liquid metal will be $2\gamma_{T,l}$ and $2\gamma_{T,l} - \gamma_{T,T}$ respectively. Although $(2\gamma_T - \gamma_{T,T})$ less than $2\gamma_T$ since usually $\gamma_{T,T} \approx \frac{1}{3}\gamma_T$ [367, 389] still at low temperatures the increased grain boundary energy in comparison to the grain volume is not as great as the higher strength. That is, the decisive factor is not their nonequilibrium state in the thermodynamic sense, but rather their ability to withstand a higher load. The analogy with a work-hardened metal, the free energy of which is higher than annealed metal, although the strength of the former is greater than that of the latter, is applicable. In connection with this at low temperature in an inert medium, a polycrystalline metal ruptures through the body of a grain.

When the same metal is acted upon by a liquid metal, $(2\gamma_{T,l} - \gamma_{T,T}) < 2\gamma_{T,l}$, since $\gamma_{T,l} < \gamma_T$. In this case, the nonequilibrium state of the grain boundaries is decisive, so that a crack develops between crystallites. Incidentally, it can be shown that the second inequality is more strongly expressed than the first, if the first is divided by $2\gamma_T$, the second by $2\gamma_{T,l}$. Then, assuming that the left portion of the first inequality is greater than the left portion of the second, we find $1/\gamma_{T,l} > 1/\gamma_T$, which is true according to the condition.)

At high temperature, polycrystalline metals rupture between crystallites in the inert medium as well [146, 268, 390]; a liquid metal medium therefore causes no change in the nature of rupture of the metal, nearly facilitating more rapid development of inter-crystallite cracks.

Let us now present the results of certain experimental investigations revealing the various specifics of the mechanism of the adsorption influence of liquid metals on solid metals during the process of deformation.

2. Regularities of Change in Characteristics of Long Term Strength and Creep of Metals Underneath the Influence of Adsorption

The regularities of the influence of adsorption-active liquid metal on solid metal during the process of creep can be analyzed on the basis of experimental data for EI437B nickel alloy. This alloy has been tested for creep to rupture, that is the test were tests for long term strength as well. The influence of liquid sodium on the alloy was investigated [391]. The tests were performed using turned tubular specimens with external diameter 11 mm and wall thickness 0.5 mm.

The specimens were filled with liquid sodium filtered at 120-130° C, providing for an oxygen content of about 0.01 wt. %. After the specimens were filled, plugs made of the same material, as the specimen were welded on in order to seal the volume containing the liquid sodium during the tests. Thus, in contrast to the more commonly used experimental methods involving specimens with surface coatings or tests in open liquid metal baths, in this case the physical and chemical properties of the liquid metal could not change as a result of interactions with components in the air. In addition to the specimens filled with sodium, control specimens filled with argon were also tested. (Subsequently, we will arbitrarily refer to these specimens at this being tested in air, and will refer to the specimens containing sodium as having been tested in sodium.)

Long term strength tests of alloy EI437B in liquid sodium and in air were performed with monoaxial extension using the ordinary method. The deformation of specimens in the process of creep was recorded using circular dial type indicators. All tests were performed at 800° C.

Figure 129 shows the dependence of time to rupture of specimens in air and in liquid sodium on applied stress. It follows from the graph that the liquid metal medium causes a significant decrease in long term strength of the alloy, the effect of its influence increasing with decreasing stress. Since the exponential dependence between time to rupture and stress is observed in both cases, the effect of the adsorption influence of the liquid metal can be characterized by the equation

$K_{\sigma D} = A \cdot \tau^{1/n-1/n_0}$, where $K_{\sigma D}$ is the coefficient of the influence of the liquid metal on the long term strength of the solid metal (see Chapter II, Section 1).

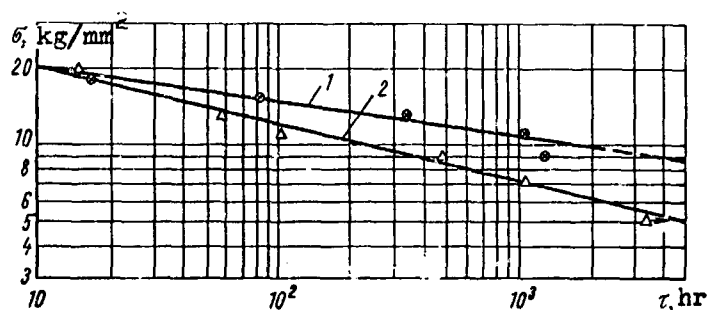


Figure 129. Time to rupture as a function of applied stress for alloy EI437B at 800°C in air (1) and in the liquid sodium (2).

The creep characteristics were also significantly changed when the alloy was tested in liquid metal. These changes can be clearly seen, for example, from the graphs of the dependence of duration of the first creep period τ_1 , the second creep period

τ_2 and the third creep period τ_3 , as well as relative elongation during each period δ_1 , δ_2 , and δ_3 resulting from the stress (Figure 130). We can see from the figure that the duration of all periods of creep is decreased in the liquid sodium medium; the relative elongation accumulated by a specimen during the first and second periods was found to be identical in sodium and in air; however, during the third period the relative elongation in the liquid metal decreased sharply. All of these changes increase with decreasing stress. The dependence shown on Figure 130 represents the schematic curves of solid metal creep in an inert medium and in a surface active liquid metal with identical stress, as shown on Figure 131.

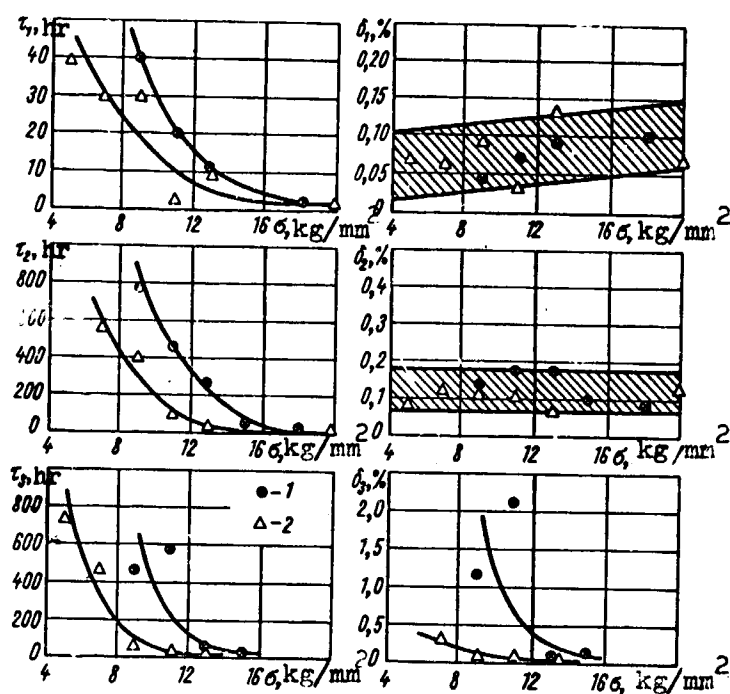


Figure 130. Duration of individual creep periods and relative elongation as functions of stress for EI437B alloy at 800° C in air (1) and in sodium (2).

The liquid sodium caused an essential increase in the creep rate of EI437B alloy. Figure 132 shows the dependence of the stable creep rate on stress in liquid metal and in air. We can see from the graph that the adsorption effect of the medium on the creep process increases with decreasing stress. The dependences of the mean velocities on stress for the first ($v_1 = \delta_1 / \tau_1$) and third ($v_3 = \delta_3 / \tau_3$) creep periods were constructed. It was found that the liquid metal causes an increase in the creep rate both at the beginning and at the end of the process. Furthermore, it was established that an exponential dependence is observed between the mean creep rate in the first period and the stress, just as in the second period (at least within the rate intervals studied).

In correspondence with the above the adsorption influence of liquid metal is characterized by the following expression for the coefficient of increased creep rate: $K_v = C \cdot \sigma^{-m}$, where

σ is the stress; C_* , m and m_l are constants (see Chapter III, Section 1).

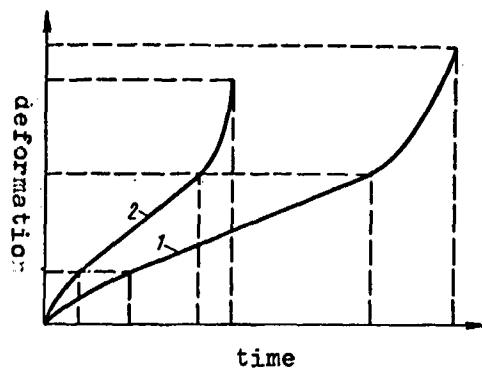


Figure 131. Diagram of change in creep curve of metal caused by adsorption influence of liquid metal medium: 1, in air; 2, in liquid metal.

There is interest in a comparison of the values of the coefficients of increased creep rate in liquid metal in the first, second and third periods on one graph. This comparison (Figure 133) shows that the liquid metal medium has the least influence on the stable creep rate, and influences the creep rate in the first and third periods much more sharply.

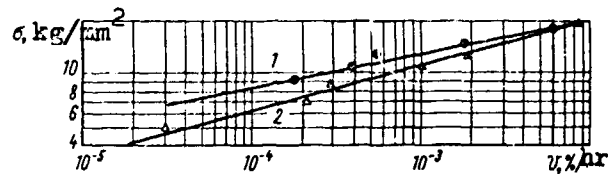


Figure 132. Rate of stable creep as a function of stress for EI437B alloy at a 800°C in air (1) and in sodium (2).

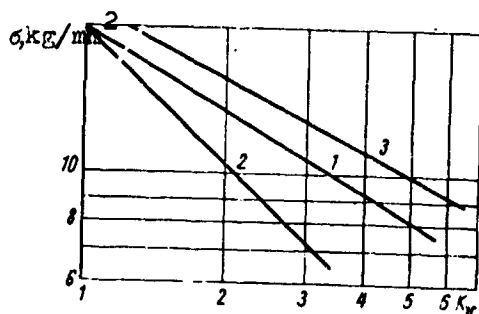


Figure 133. Coefficient of increased creep rate as a function of stress for EI437B alloy in liquid sodium at 800°C : 1, K_{v1} ; 2, K_{v2} ; 3, K_{v3} .

The effects which we have described in the influence of liquid sodium on long term strength and creep of EI437B alloy result from adsorption. In order to test for corrosion damage of the specimens, microsections were prepared after rupture. Microstructural analysis showed no traces of corrosion effects of the liquid metal. Spectral analysis confirmed the absence of diffusion of sodium into the alloy. Thus, the influence of the liquid metal in this case results completely from its ability to decrease the surface interface energy at the boundary between the solid and the liquid metals. This would be expected, for example, on the basis of data on "wettability" reference [158]. It should also be emphasized that the conditions of performance of the experiments (grain size of material - 2-3 grains in cross section of specimen) facilitated appearance of the adsorption effect of the medium [392].

The effects of the adsorption influence of the liquid metal correspond to the existing dislocation concept concerning the processes of creep and rupture of metals [381-383, 393, 394]. Let us attempt first of all to explain why the adsorption-active medium causes an increase in the creep rate which is much sharper in the first period than in the second period. At first, immediately after loading of the specimen, a large number of dislocations begin to move. The rate of plastic deformation in this case is determined by the rate of movement of the dislocations and the influence of applied stress. As time passes, the number of moving dislocations decreases, since some of them are held up by the various obstacles. Certain obstacles were already present in the structure of the metal before the beginning of deformation, while others arose as a result of deformation (for example, dispersive separation of the second phase, packing defects, interstitial atoms, steps at dislocations, stress fields of other dislocations, etc). As a result of this, the creep rate drops gradually and, finally reaches its equilibrium value, characteristic for the second creep period. During this period, if creep occurs at high temperature, further displacement of dislocations is possible only after creeping over into a neighboring slipping plane, where obstacles on the creeping path (or a portion of the path) are absent. The process of creep over is a diffusion process, and its activation energy is equal to the activation energy of self diffusion. If the creep occurs at low temperature, the activation energy of the creep is less than the activation energy of self-diffusion and depends on the value of stress applied (decreases with increasing stress).

Thus, with both high and low temperature creep the difference between the values of the energy barriers which the dislocations overcome as they move within the metal and come to the free surface are greater for the second creep period than for the

first period. This means, according to the preceding section, that the degree of the influence of the surface active liquid metal on the first period should be greater than on the second period.

Obviously, the increase in the adsorption influence of the medium at the beginning of creep also results from the greater activity of surface sources of dislocations. Frank-Reed sources with one point of attachment can play an essential role in this process, since they begin to act at stresses half as great as the activation stress for sources with two points of attachment. Experimental proof has been presented to indicate that plastic deformation begins in the surface layer of a crystal; for example, this has been shown by the well known experiments of Suzuki [395] and of Chalmers and Davis [396]. The influence of the state of the surface on plastic deformation, including its initial stage, has been confirmed by many experiments with specimens covered with films of solid metals [397].

The weakening of the adsorption influence of the liquid metal on a solid metal upon transition from the first stage of creep to the second stage is also confirmed by the results of relaxation tests of steel in liquid sodium [398]. It is then established that in this case the influence of liquid metal on the process of relaxation of stresses decreases with passing time. If we consider that relaxation is creep with decreasing stress, it should be expected that the physical processes forming the two phenomenon would be identical. The decrease of stress in relaxation tests can lead to an increase in activation energy of displacement of dislocations in comparison with its value during creep tests under stress maintained equal to the initial stress upon relaxation. (The following dependence of activation energy on stress τ_s is considered correct: $Q = Q_0 - Ab\tau_s$, where b is the Burger vector; A is the area of the surface covered by the dislocation.) Therefore, the time dependence of the adsorption effect in tests with relaxation should be expressed even more sharply than in tests with creep.

Figure 133 shows that the adsorption effect of sodium on the alloy is reinforced once more in the third creep period. This peculiarity of the influence of the liquid metal can be understood if we consider that in addition to the deformation processes, cracks develop under creep conditions. As time passes, both the number of cracks and their length increase. Furthermore, the rate of growth of cracks increases [399-402]. It is also characteristic that all of these changes are particularly sharply expressed during the third creep period. Therefore, the reinforcement of the adsorption effect can be caused by the following

factor: first of all, by an increase in the number and length of cracks, leading to an increase in the effective stress and causing an increase in the number of active dislocations; secondly, by the fact that the surface active metal facilitates acceleration of the development of the cracks themselves, which is reflected in the total value of relative elongation (an important part of the relative elongation of the specimen during the third period is a result of increasing velocity [401]). The specific nature of the third creep period related to the intensive development of cracks is also reflected in the fact that the plasticity during the third period in liquid metal is less than air, whereas during the first and second periods the plasticity is identical in the two media.

The effect of the increased adsorption influence of the liquid metal with decreased stress described above is apparently related to the decreased rate of movement of dislocations in this case. The dependence of the mean rate of movement of boundary dislocations v on applied stress τ_s in reference [403] can be represented in the form

$$v = v_0 e^{-\beta/\tau_s^2}, \quad (218)$$

where v_0 is the maximum possible rate of movement of dislocations equal to the speed of sound in the metal; β is a constant.

Formula (218) allows us to calculate the mean rate of dislocations with constant stress. However in various sectors of the crystal individual dislocations move at different speeds, as a result of the influence of local stresses, which may be either higher or lower than the applied stress. Therefore, and in consideration of the factors outlined in the preceding section, one group of dislocations with mean velocity \bar{v}_1 will not

experience the influence of the liquid metal as it arrives at the surface; the mean velocity of dislocations of another group were increased to the maximum under the influence of the medium (from \bar{v}_2 to $\bar{v}_{2\ell}$) and, finally, the mean velocity of dislocations of

the third group will increase but to a lower degree than the velocity of the second group (from the \bar{v}_3 to $\bar{v}_{3\ell}$). Obviously

in connection with (218), the following inequalities will be fulfilled: $\bar{v}_1 > \bar{v}_3 > \bar{v}_2$ and $\bar{v}_1 > \bar{v}_{3\ell} > \bar{v}_{2\ell}$. If we represent

the dislocation density as n , its partial values corresponding to each group of dislocations n_1 , n_2 and n_3 , and the Burger vector

as b , the creep rate in an inert medium is expressed by $\dot{\epsilon} =$

$= b[n_1\bar{v}_1 + n_2\bar{v}_2 + n_3\bar{v}_3]$, while the creep rate in the liquid

metal $\dot{\epsilon}_L = b[n_1\bar{v}_1 + n_2\bar{v}_2 + n_3\bar{v}_3]$. Since the $\bar{v}_{2L} > \bar{v}_2$ and $\bar{v}_{3L} > \bar{v}_3$, we produce $\dot{\epsilon}_L > \dot{\epsilon}$.

As the applied stress is changed, the values of the differences $(\bar{v}_{2L} - \bar{v}_2)$ and $(\bar{v}_{3L} - \bar{v}_3)$ will change, as will the number of dislocations in each group. Increasing the stress first leads to a decrease in the values of n_2 , then to complete disappearance of the second group of dislocations and, finally, at a certain critical stress value, the adsorption effect of the medium appears no longer.

3. Adsorption Effect with Deformation by Compressive Load

In works on the investigation of the influence of a liquid metal medium on a solid metal in the stressed state it is generally emphasized that this influence appears in the presence of tensile stresses. For example, tests with short term bending have demonstrated that the strength and plasticity of solid metals do not change if the liquid metal is applied to the compressed side of the specimen (see Chapter I, Section 1). However, on the basis of the concepts concerning the mechanism of the influence of an adsorption active liquid metal medium on the process of deformation of a solid metal which we have presented, we would expect the medium to have an influence during compression as well. Naturally, if the adsorption effect is related to facilitation of movement of dislocations to the surface of the specimen as a result of decreased resurface energy of the steps formed, it should be observed during compressive stress as well.

In order to check this assumption, the influence of liquid metal on the process of creep during monoaxial compression was studied [404]. The combination of solid copper (type M-1) and liquid bismuth was selected for the experiments, since the presence of adsorption effects in this system is beyond doubt. As we know, in liquid bismuth a significant reduction of the free surface energy of solid copper occurs [111], and a decrease in plasticity of copper in contact with this liquid metal has been observed repeatedly [8, 405].

Tests were performed with tubular cylindrical specimens* with a wall thickness of 0.5 mm and an internal diameter of 10 mm.

*Specimens tested after annealing for two hours at 600° C in a vacuum (about 10⁻⁴ mm Hg).

The liquid metal was contained inside the specimen; the working volume was sealed by welding on caps. The specimens were tested for creep using type UIM-5 machines. Loading of the specimens with a compressive load was achieved using a reverser. Identical specimens were also used to perform tensile tests for comparison with results of the compressive creep tests. All creep tests were performed at 350° C. The stresses used in the tensile tests were lower than in the compressive tests since when high tensile loads were applied the specimens in contact with the liquid bismuth were ruptured at the moment of application of the load.

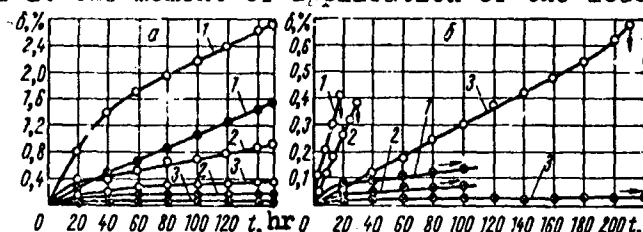


Figure 134. Curves of creep of copper at 350° C in liquid bismuth (O) and air (⊙):
a - compression; 1 - $\sigma = -4 \text{ kg/mm}^2$;
2 - $\sigma = -3 \text{ kg/mm}^2$; 3 - $\sigma = -2 \text{ kg/mm}^2$;
b - extensions; 1 - $\sigma = 1.8 \text{ kg/mm}^2$;
2 - $\sigma = 1.5 \text{ kg/mm}^2$; 3 - $\sigma = 1.0 \text{ kg/mm}^2$.

Figure 134 shows creep curves in air and in liquid bismuth for compressive and tensile stresses. We can see from the graphs that the creep of copper in liquid bismuth occurs more rapidly than in air, both in extension and in compression. One common feature of the influence of the liquid metal medium in both cases is the fact that as stress decreases, relative influence of the medium increases. The difference lies in the absolute values of deformation, in the relative strength of the influence of the medium and in the fact that during extension in liquid bismuth, even in extremely low stresses, creep goes over into the third period and the specimen is ruptured.

Figure 135 shows the dependence of the rate of stable creep on stress. These dependences indicate that during compression and extension the dependence between these quantities is logarithmic and that this is true for tests in air and in the liquid metal medium. The degree of influence of the liquid metal medium is different in extension and in compression: in extension, the liquid bismuth causes a considerably greater increase in creep rate than in compression (with identical stress values). It is also characteristic that the difference in creep rates in air and in liquid metal is greater, the lower the applied stress (Table 51).

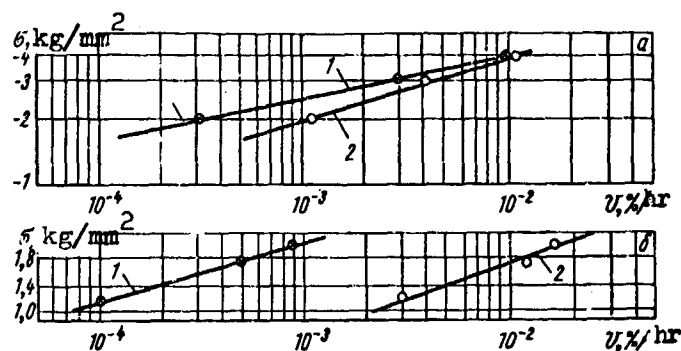


Figure 135. Stable creep as a function of stress for copper at 350° C in air (1) and in liquid bismuth (2): a - compression; b - extension.

Thus, a surface active liquid metal influencing the process of deformation in extension also influences the process of deformation in compression. The nature of the influence is identical in both cases, but the degree of influence is higher in extension. The greater increase in creep rate in the liquid metal in extension than in compression is explained apparently by the fact that during extension rupture cracks are formed and developed, while during compression the deformation process occurs without formation of cracks (at least in the material tested for the values of deformation covered by the experiments). Consequently, in compression the liquid metal has an influence only on the process of deformation, while in extension it also influences the process of rupture and the process of crack development.

Table 51

Results of Creep Tests of Type
M-1 copper at 350° C in Liquid
Bismuth and in Air

Type of Test	Stress, kg/mm ²	Ratio of Creep Rates in Bismuth and in Air
Compression	- 4	1.1
	- 3	1.4
	- 2	3.8
Extension	+ 1.8	18.2
	+ 1.5	26.0
	+ 1.0	30.0

4. Adsorption Effects as Functions of Free Energy of Solid-Liquid Metal Boundary

The adsorption nature of the influence of liquid metal on solid metal is particularly clearly seen when the change in free energy of the solid-liquid metal boundary is established by direct experiments. Figure 136 shows the dependence of the energy of the solid copper-liquid metal Bi - Pb alloy boundary on the composition of the alloy at 350° C [8]. The graph shows a continuous decrease in surface energy with changing alloy composition: from 390 erg/cm² for a boundary with pure lead to 280 erg/cm² with pure bismuth. The decrease in surface energy is particularly sharply noted in the lead concentration interval from 80 to 40%.

Work [8] presents the results of tests of copper for short term rupture in the Bi - Pb melts. It was found that the change in the tensile strength and relative elongation depended strictly on the change in surface energy as the composition of the liquid metal was changed, proving the adsorption origin of the effects observed. This conclusion would be even more convincing and general if a similar regularity were produced with another type of test. Therefore, copper was tested for creep and long term strength in Bi - Pb alloys of varying compositions [406].

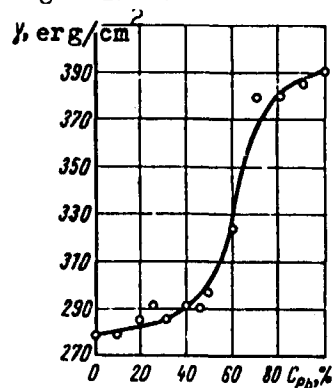


Figure 136. Free interphase energy of boundary of copper with Bi - Pb alloys at 350° C.

The tests were performed with monoaxial extension of tubular turned specimens with wall thickness 0.5 mm using the methodology described above. The specimens were prepared of M-1 copper, annealed at 600° C for two hours in a vacuum of about 10⁻⁴ mm Hg.

All tests for long term strength and creep were performed at stresses of 5 kg/mm² and 350° C. The time to rupture of the copper as a function of liquid metal composition was represented on the graph of Figure 137 a. We can see that the lifetime of a specimen under constant load decreases regularly with an increase in the content of bismuth in the melt. The amount of this increase is significant; for example, whereas the time to rupture in lead is 540 hours, in liquid bismuth a specimen is ruptured

after 17 hours. It is characteristic that the form of a long term strength curve on Figure 137 a is similar to the curve of interphase energy shown on Figure 136. The sharp change in time to rupture curves as the content of lead in the alloy is varied between 40 and 80%, that is in the same interval where the interphase energy changes sharply.

Figure 137, b shows the relative elongation of specimens up to the moment of rupture as a function of liquid metal medium composition. We can see from the graph that as the content of bismuth in the alloy increases, that is as the surface interphase energy decreases, the plasticity of the copper decreases continually. The relative elongation of the specimen tested in lead is 14.95%, in bismuth - 2.69%. In this case as well, the curve of Figure 137, b is similar to the curve of Figure 136.

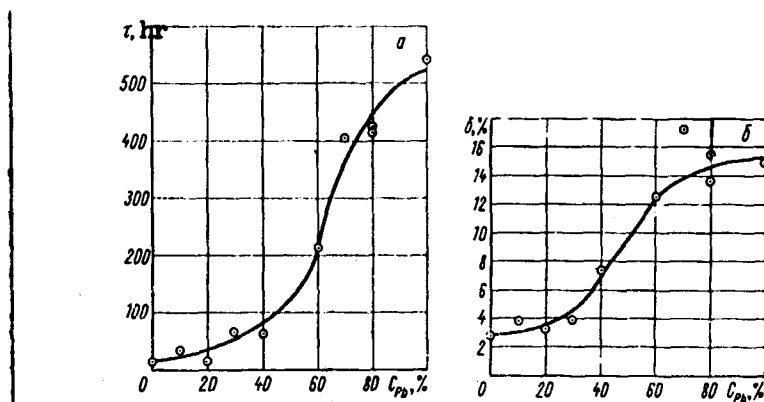


Figure 137. Time to rupture (a) and relative elongation (b) of copper specimens tested for long term strength at 5 kg/mm² stress and 350° C in Bi - Pb alloys.

The influence of the composition of the liquid metal medium and consequently of the interphase energy on the creep rate of copper is shown on Figure 138. A decrease in interphase energy causes an increase in the creep rate of the copper. The influence of the medium is reflected both on the stable creep rate (Figure 138 a), and on the mean creep rate during the first period (Figure 138, b). In order to establish whether the influence of the liquid metal is greater at the beginning of the creep process or during the stable stage, the dependence of the ratio of creep rates of copper in Bi - Pb alloys with a corresponding creep rates in pure lead was constructed (Figure 139). It follows from this dependence that the surface of active liquid metal causes a

greater increase in creep rate at the beginning of the process, that is in its first period, and in the second period. Furthermore, Figure 139 shows that the degree of the influence on creep, as well as the difference in the degree of the influence in the first and second periods increase with increasing surface activity of the liquid metal medium.

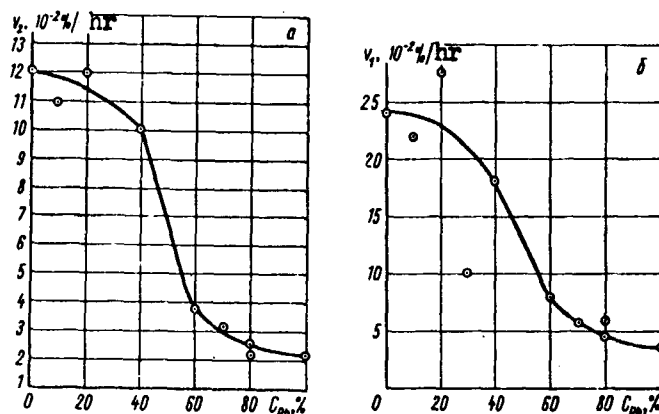


Figure 138. Rate of stable creep (a) and mean creep rate in the first period (b) of copper specimens at 5 kg/mm^2 stress and 350°C in Bi - Pb alloys

Thus, the experimental data presented above show clearly that a decrease in interphase energy at the solid metal-liquid metal boundary causes a regular decrease in long term strength and plasticity and an increase in the solid metal creep rate. Consequently, they indicate reliably an adsorption influence of the liquid metal on the processes of deformation and rupture under the conditions of testing of the material for creep and long term strength.

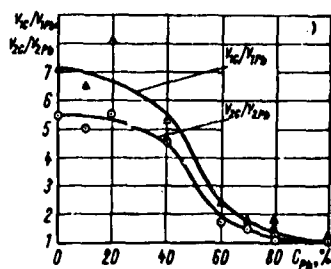


Figure 139. Ratio of creep rate of copper specimens in the first and second periods in Bi - Pb alloys to creep rate in pure lead.

We indicated earlier that the liquid metal medium causes the number and length of cracks formed in the structure of the metal deformed to increase, and causes a change in the nature of a rupture -- a transition from intracrystallite to intercrystallite rupture. It seemed of interest to determine whether finer changes in the structure occurred under the influence of the adsorption active liquid metal. These changes should be expected due to the intensification of the process of plastic deformation, particularly in the surface layer of the metal.

The influence of organic surface active media, manifested as a decrease in the thickness of slipping units and an increase in their number [37], as well as an increase in dislocation density [402], has been experimentally established. In order to determine the influence of liquid metal, X-ray structural studies of the surface layer of copper specimens were performed after long term strength tests in Bi - Pb alloys*. Plates 3 mm wide and 12 mm long (the long side corresponding to the generatrices of the gauge portion of the specimen) were cut from the specimens for which the results of mechanical tests are presented in Figures 137-139. In order to remove traces of the low-melting metal from the surface of the plates, they were etched in 10% aqueous HNO_3 . Irradiation (Cu_α) of the specimens was performed using a URS-50I apparatus. During irradiation, the specimen was rotated at 2 rpm. The X-ray reflections from the (311) plane were recorded, and the changes in the intensity of the corresponding line were used to determine III order distortions in the structure of the metal. The reflections from plane (311) of an annealed copper specimen were used as a standard.

In order to differentiate the influence of the liquid metal on the intensity of the (311) line from the influence of the plastic deformation occurring in the specimen in an inert medium using the same load as in the experiments, this line was recorded for the external and internal surfaces of the copper plate.

New results of measurement of the intensity of line (311) are presented on Figure 140. We can see from this figure that the intensity of X-ray interference from the same plane changes differently depending on the composition of the medium for the external (air side) and internal (liquid bismuth side) surfaces. The change in intensity of the first case obviously indicates the influence of the duration of test time on III order distortions. Comparison of Figure 140 a and 137 a indicates that these distortions increase as the loading time of the specimen increases.

* X-ray tests performed by G. D. Pigrova.

The decrease in the intensity of X-ray interference from the internal surface of the specimens tested in alloys with high bismuth content indicates the increased distortion of the structure in volumes on the order of the dimensions of a unit cell under the influence of the surface active liquid metal. These distortions are on the order of the crystalline lattice constant of the specimen. The coincidence of the right parts of the two lines of Figure 140 a indicates the identical influence (or absence of all influence) of the air medium and alloys with high lead content and pure lead.

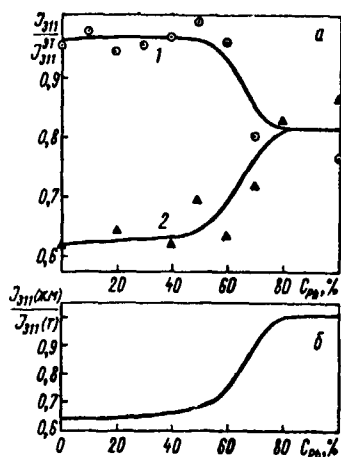


Figure 140. a - Ratio of intensity of (311) line for external (1) and internal (2) surfaces of copper specimens tested for long term strength in Bi-Pb alloys to intensity of same line for annealed copper; b - Ratio of intensities of (311) line for internal surfaces of specimen to intensity of the same line for external surface.

In connection with the fact that the intensity of X-ray interference from the external surface can be looked upon as a standard for determination of the adsorption effect of the liquid metal, this influence can be judged by the ratio of intensities of the lines for the internal surface $I_{311} (L)$ and external surface $I_{311} (T)$ (see Figure 140 b).

Comparing Figure 140 b with Figures 137-139, we conclude that the adsorption effect of the liquid metal leads to the formation of III order distortions in the metal structure tested for creep.

5. The Reason for Differences in the Nature of the Adsorption Influence of Liquid Metals and Organic Materials

The most important difference in the adsorption effects of organic and liquid metal media on the deformable metals lies in the absence of brittle rupture of metals in organic media, since

this form of rupture is a characteristic feature of melted metals. This difference was first noted by Ye. D. Shchukin and P. A. Rebin-der [344]. They indicate that the differing nature of the influence of surface active organic and liquid metal media is related to the essentially greater decrease in free surface energy of the solid metal in liquid metal media. Thus, whereas in liquid metals the decrease in surface energy may amount to some hundredths of ergs per 1 cm^2 , in organic media it amounts to but some dozens of ergs. In certain cases, the increase in the adsorption effect of liquid metals is related to rapid penetration of the adsorption active atoms to the surfaces of internal micro cavities by two dimensional migration along defects in crystalline structure [344]. It was noted at the same time that the plasticizing effect of organic adsorption active media is based on their surface interaction with the specimen, which leads to a decrease in the potential barrier preventing movement of dislocations the surface of the crystal, and the formation of a new surface; it was considered that the plasticizing effect of liquid metal media cannot be explained in the same way [344].

The experimental material which has been accumulated at the present time allows us to state an additional consideration concerning the reasons for the differing manifestations of adsorption effects of liquid metal and organic media.

First of all, we should note the fact that the results of tests of materials for long term strength and creep in surface active liquid metal media presented above (Chapter V, Section 2-4) indicates simultaneous occurrence of effects of facilitation of plastic deformation (increased creep rate), embrittlement (decrease in total relative elongation at rupture) and decreased strength (long term strength). These results were produced in experiments with polycrystalline metals, but the results would apparently be the same for monocrystals if the specimens in experiments on creep (see Chapter III, Section 1) were subjected to testing to rupture.

Furthermore, if we look at the results of tests in extension at constant velocity, we can conclude that the changes in the stress-strain diagrams in organic [3] and liquid metal (see Chapter I, Section 1) media in comparison to the diagrams in an inactive medium are similar: in both cases the yield point, hardening factor and strength are decreased. The differences only that the relative elongation of the metal is greater in tests with an organic surface active agent than in tests with an inert medium, while it is less in tests with liquid metal surfactant.

These facts indicate that liquid metals accelerate the process of rupture to a greater extent than do organic surfactants. The large molecules of the organic materials cannot penetrate into the submicrofissures or to the ends of micro- and macrofissures. The small dimensions of cracks, as was indicated earlier in [47], represent a steric obstacle. The atoms of liquid metals, on the other hand, can penetrate into the smallest defects in the structure of the solid metal. Therefore, the process of rupture in a liquid metal medium occurs incomparably more intensively than in an organic surface active agent.

The acceleration of the process of deformation in both media occurs as a result of interaction of atoms of the solid and liquid metals at the points where dislocations reach the surface or as a result of the corresponding decrease in surface energy of the step formed at this point. The intensity of the influence of the medium in this case is apparently independent of the dimensions of the molecules and atoms, and is determined only by their mobility and the degree of the decrease in surface energy.

Thus, the practically identical effect of surface active organic and liquid metal agents on the process of deformation results in an identical manifestation - facilitation of the process of deformation (decrease in yield point and hardening factor in extension at constant rate and increase in creep rate under constant load). Consequently, the effect of facilitation of deformation is a universal effect, characteristic for various surface active agents.

The difference in organic media from liquid metal media is the greater acceleration of the process of rupture in liquid metal than in the organic media. This difference is manifested as a significant decrease in plasticity in the liquid metal in comparison to the inactive media. The effect of embrittlement also appears in extension with constant rate and under conditions of long term strength testing. In organic media the metal is deformed to a considerably greater extent before rupture than in an inactive medium.

Consequently, the differing influence of organic and liquid metal surface active agents on the process of rupture and their identical influence on the process of deformation means that rupture of a metal in an organic medium occurs later and at higher plasticity, while in a liquid metal medium it occurs earlier and with lower plasticity than in an inactive medium.

B. Corrosion Influence

1. Mechanism of Corrosion Influence of Liquid Metal on Solid Metal in The Process of Rupture

The corrosion influence of liquid metals on solid metals in the stressed state depends on the same corrosion processes which are observed when metals are tested in the unstressed state. That is, in this case as well, simple dissolution, thermal and isothermal mass transfer, intercrystalline corrosion and other processes are possible (see Part I). However, the manifestations of these processes in metal under stress have certain specific features.

The rupture of metal as a result of the simultaneous effects of stress and a corrosion active medium is not a result of the decrease in cross section of the specimen (part) bearing the load and the corresponding increase in effective stress alone. If materials are placed in sequence according to characteristic resistance to total corrosion (for example, according to the inverse of corrosion rate), this series will not coincide with the sequence in order of resistance to the effects of liquid metal on the stressed solid metal (for example, the sequence in order of increasing long term strength reduction factor). In particular, although certain materials undergo corrosion in liquid metal at identical rates, this does not mean that the degree of redemption of their strength under conditions of extension at constant rate or long term strength testing or fatigue testing will also be identical. For example, corrosion tests have shown [79] that the rate of thermal mass transfer of nickel-based alloys EI827, EI869 and EI765 in liquid sodium at 750° C with a temperature drop of 350° C is identical, at $2.62 \cdot 10^{-6}$ mm/hr. However, when these materials were tested for long term strength under analogous conditions, it was found that they have varying abilities to resist the corrosion effect of the liquid metal. (Control tests of the alloys in sodium under static, isothermal conditions have shown that the effect of the liquid metal in the presence of thermal mass transfer is corrosive: under isothermal conditions, the change in long term strength in relation to its level in air did not occur.) Table 52 presents values of the reduction factor for long term strength of these alloys in liquid sodium over 100 and 1000 hours. We can see from this table that the greatest resistance is that of alloy EI765, the least being that of alloy EI869, and that the values of long term strength reduction factors in 1000 hours indicate that the degree of influence of the liquid

metal medium on the former is 12% less than on the latter. In the 100 hour test, alloy EI 765 showed no changes in the level of long term strength in sodium at all, whereas the reduction of the corresponding strength of EI 869 was 26%.

Some types of corrosion influence of liquid metals on solids are more dangerous for stressed metal than others. The greatest danger is not that of the total corrosion of the material, but that of local and microlocal processes. Therefore, a material subjected to intensive intercrystalline corrosion in liquid metal in the unstressed state, for example, cannot withstand the effects of stresses.

Table 52

Values of Long Term Strength Reduction
Factors of Alloys EI827, EI826 and
EI765 in Liquid Sodium under Thermal
Mass Transfer Conditions. (Temperature
750°, Drop 350° C).

Alloy type	Medium	$\sigma_D 100$, kg/mm ²	$K_{\sigma_D 100}$	$\sigma_D 1000$, kg/mm ²	$K_{\sigma_D 1000}$
EI 869	Air	25,5	0,74	14,0	0,68
	Na	18,8		9,5	
EI 827	Air	34,5	0,80	26,0	0,71
	Na	27,5		18,5	
EI 765	Air	27,0	1,00	20,0	0,80
	Na	27,0		16,0	

The dangerous types of corrosion influence of liquid metal also include selective corrosion, particularly if the easily soluble component is horophilic. The results produced for brass (see Figure 104) indicate the influence of selective corrosion on the resistance of alloys to the effects of a liquid metal medium when tested for long term strength. Experiments have shown that with increasing content of zinc in brass -- an element easily dissolved in tin -- the long term strength decreases sharply. The conclusion of the essential influence of selective corrosion on the strength of alloys in a liquid metal medium is confirmed by the results of reference [408]. It is shown in this work that the tensile strength in extension at constant rate of 70/30 brass₂ increases to 17.3 kg/mm² in a medium of pure mercury to 23.6 kg/mm² in mercury containing 2.02% Zn. It is established in this work that the surface tension of pure mercury and its amalgams

containing 2.02% Zn is practically identical. Apparently, these facts can be looked upon as an indication of the identical value of the free interphase energy of the boundary between brass and mercury and its amalgams.

Due to the local nature of the corrosive influence of a liquid metal on a solid metal in the stressed state, specifics of the structure of the solid metal become important. Obviously, heterogeneity of the structure, the presence of phases easily dissolved in the liquid metal or entering into active physical-chemical interactions with it should cause an increase in the influence of the medium. Increased corrosion rupture of the material, related to the development of cracks, may begin at such thermal dynamically non-equilibrium sectors of the structure and grain boundaries and mosaic block boundaries, points of contact of slipping planes with the surface, etc.

The nature of the development of rupture processes of the solid metal in the inert medium is also significant. For example, if intercrystalline cracks appear in large number in the early stages of deformation, the reduction in long term strength in a corrosion active liquid metal medium will be greater than that of a metal having relatively long incubation period for the formation of cracks and smaller numbers of cracks.

As was indicated in Part I of this book, the most dangerous form of corrosion damage to materials in a liquid metal medium is thermal mass transfer. The occurrence of this process is unavoidable in principle in heat exchange installations, since they have different temperatures in different areas along the length of the heat transfer medium channel. In spite of the linear corrosion rule effective under such conditions and the absence of any acceleration or deceleration of the process, even materials subjected to even dissolution when stresses do not act upon them will show an essential increase in the effect of the influence of the medium in the stressed state due to the occurrence of local corrosion processes.

This conclusion has been confirmed, for example, by the results of tests for long term strength of type EI869 nickel-based alloy in liquid sodium [276, 409]. The tests were performed at 750° C in a current of the liquid metal using a method described in Chapter II, Section 1. During the tests, a flow of sodium moving through the internal cavity of the tubular specimens by natural convection arising due to the temperature drop maintained (in this case 350° C) through the height of the liquid metal column acted upon the material. Under these conditions, the process of thermal mass transfer of the material of the gauge section of the specimen in the "hot" zone up to the higher "cold" zone is continuous.

Tests of alloy EI869 showed that its long term strength is significantly decreased as a result of the thermal mass transfer (Figure 141). It is important to note that the effect was in entirely a result of thermal mass transfer: the absence of adsorption and diffusion effects of the medium was indicated by the correspondence of the results of the test in sodium under isothermal conditions and in air (see Figure 141). The microstructural study of the specimen after rupture establish that the liquid metal causes no structural changes in the alloy. Corrosion tests of the alloy in the unstressed state under the same conditions demonstrated [78] that intercrystalline corrosion of the specimen does not occur. Therefore, it can be assumed that the reason for the decrease in long term strength is the effect of reduction in cross sectional areas of the specimen. The influence of this effect can be easily evaluated by using the hypothesis of linear addition of damage, which yields satisfactory correspondence of calculated quantities to experimental values [410-414]. The initial dependence with this estimate is the relationship

$$\int_0^{\tau_R} \frac{dt}{\tau_0} = 1, \quad (219)$$

where t is the current time; τ_0 is the time to rupture with constant stress; in this case the constant stress acts on the specimen over time dt ; τ_k is the time to rupture with variable stress, provided in these experiments by thermal mass transfer.

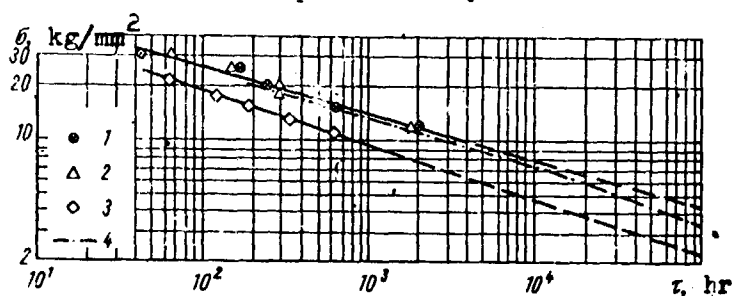


Figure 141. Diagram of long term strength of EI869 alloy at 750° C;
1 - tests in air; 2 - in sodium (static isothermal conditions); 3 - in a convective current of sodium; 4 - calculated dependence.

The stress value for the tubular specimen which we use can be approximately expressed in the form

$$\sigma \approx \frac{P}{\pi D (\delta_0 - kt)}, \quad (220)$$

where P is the load; D is the external diameter of the specimen; δ_0 is the initial wall thickness of the specimen; k is a coefficient characterizing the rate of mass transfer, determined from equation $q = kt$, where q is the depth of corrosion in time t .

Using relationships (219) and (220), as well as the dependence between time to rupture and stress with no influence of the medium $\tau_0 = A_0 \sigma^{-n_0}$, we arrived at the following equation:

$$\frac{1}{A_0} \left(\frac{P}{\pi D} \right)^{n_0} \int_0^{\tau_k} (\delta_0 - kt)^{-n_0} dt = 1. \quad (221)$$

The integral in equation (221) can be easily selected using the substitution $x = (\delta_0 - kt)^{1/r}$, where r is the denominator of fraction n_0 . We finally produce the following expression for the time to rupture of the material in the presence of thermal mass transfer as a dependence on initial stress:

$$\tau_k = \frac{1}{k} \{ \delta_0^{1-n_0} - A_0 k (n_0 - 1) \delta_0^{-n_0} \sigma^{-n_0} \}^{\frac{1}{1-n_0}}. \quad (222)$$

It follows from equation (222) that the time to rupture of a material in a convective flow of heat transfer medium, τ_k and the time without the influence of the medium τ_0 should be related by the following expression

$$\tau_k = \frac{1}{k} \{ \delta_0^{1-n_0} - k (n_0 - 1) \delta_0^{-n_0} \tau_0^{\frac{1}{1-n_0}} \}. \quad (223)$$

Let us determine the quantitative relationship of the experimental and calculated depth. We will do this by calculating the time to rupture of specimens of alloy EI869 in a convective heat flow, using formula (223). From the long term strength diagram (see Figure 141) we find that $n_0 = 3.76$. On the basis of [79], $k = 2.62 \times 10^{-6}$ mm/hr. The initial wall thickness of the tubular specimen (δ_0) in our experiments was 0.5 mm. Thus, equation (223) as applicable to EI869 alloy tested in sodium at 750° C has the form

$$\tau_k = 3.8 \cdot 10^5 [0.5 - (6.75 + 9.8 \cdot 10^{-5} \tau_0)^{-0.362}]. \quad (224)$$

In connection with the specifics of the structure of equation (224), significant errors in the calculation of τ_k can arise with small values of τ_0 ; therefore, we will perform the

calculation for τ_0 equal to 10^3 , 10^4 and 10^5 hr. The results of calculations are presented in Table 53. This same table shows the experimental values of τ_k^e produced from the long term strength diagram shown on Figure 141.

Table 53

Calculated and Experimental Values of
Time to Rupture of Alloy EI869 in
Convective Flow of Sodium at 750° C.

τ_0 , hr	τ_R , hr	τ_R/τ_0	τ_R^e , hr	τ_R^e/τ_0
10^3	950	0,95	260	0,26
10^4	8560	0,86	2000	0,20
10^5	52400	0,52	15000	0,15

We can see from the table that the effect of decreased long term strength of alloy EI869 observed in a convective flow of sodium is considerably greater than that which should be expected on the basis of the calculations. The difference between the calculated and experimental data can also be clearly seen from the long term strength diagram (see Figure 141). This result can only be explained by the fact that the decrease in cross sectional area of the specimen occurring as a result of the process of mass transfer is not the main reason for the decrease in long term strength of the material.

Thus, the experimental data currently available convince us of the local nature of the corrosion effect of the liquid metal. Obviously, the decrease in strength of a solid metal in a corrosion active liquid metal is determined by physical and chemical processes of their interaction in the end portion of a crack. Analyzing this interaction in its general form, it can be characterized by a certain mean specific work of interaction of the medium and base metal over the length of the crack χ . Then the expression for the change in energy of the metal when a crack of length c is formed in it is written, similarly to (180) in the form

$$\Delta E = 2\gamma c + pc - \chi c - \sigma^2 c^2 / 2E. \quad (225)$$

From equation (225), considering that the relationship $d \Delta E / dc = 0$ is correct for the critical state of the crack, we

we produce

$$\sigma_n = \mu \sqrt{\frac{E(\gamma + p/2 - \kappa/2)}{c}}. \quad (226)$$

Consequently, the rupture resistance of the metal decreases with increasing corrosion influence of the solid and liquid metals (that is with increase in value of κ).

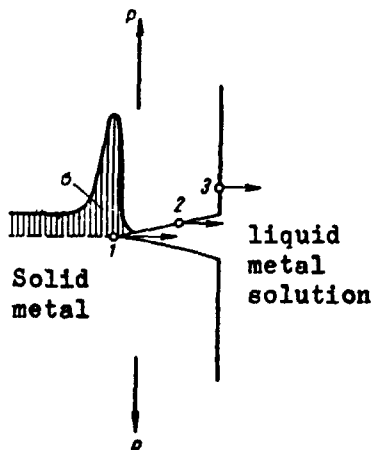


Figure 152. Diagram for explanation of greater probability of transition to liquid metal solution of atoms located in end portion of crack (1) than of atoms in neighboring portions of surface (2 and 3).
(P equal load, σ equal stress)

The influence of the liquid metal on the process of rupture of the solid metal under the conditions of tests for long term strength and other forms of tests with thermal mass transfer can be described using the diagram shown on Figure 142. Since there is always a concentration of stresses in the end area of the crack, the atoms in this area are of essentially higher potential energy than atoms in neighboring sectors of the crack and on the remaining surface of the metal. Consequently, the probability of transition to the liquid metal solution of the former is considerably greater than that of the latter. Therefore, with comparatively low rate of general corrosion (mass transfer), considerable localization of corrosion in the end portion of the crack is possible. One result of this acceleration of the process of dissolution is rupture of some atomic bonds and weakening of others, which in the final analysis causes an increase in the rate of crack development and a decrease in the time to rupture of the metal.

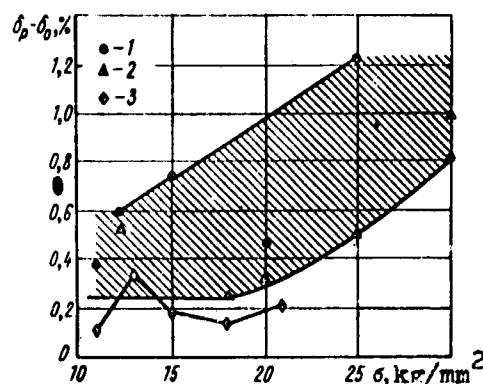


Figure 143. Dependence of relative elongation accumulated by EI869 alloy in the process of creep to rupture on stress. Temperatures 750° C: 1 - tested in air; 2 - in sodium, isothermal static conditions; 3 - in convective sodium flux.

The effect of decreasing plastic deformation accumulated by the specimen over the time to rupture is also related to the increasing rate of crack growth. The decrease in total plastic EI869 alloy when tested for long term strength in sodium in the presence of thermal mass transfer can be seen from Figure 143.

Comparing the corrosive influence of a liquid metal medium to the adsorption influence, we should note that whereas the adsorption effects can be observed almost immediately after contact arises between the medium and the deformed metal, the appearance of corrosion effects requires a certain amount of time, involving the development of physical and chemical processes causing irreversible structural changes in the metal. Therefore, the corrosion influence may not appear with short term mechanical tests of metals but may cause an essential decrease in their strength and plasticity with longer tests - in experiments for long term strength and fatigue. For this same reason, an increase in the corrosive effect of the medium should be expected with a decrease in the frequency of a fatigue test if the amplitude of the stress (deformation) remains unchanged.

The lower dependence of the adsorption effect of a liquid metal on time in many cases causes a catastrophic drop in strength and plasticity of the material when it is deformed even at very high rates. Since the diffusion effect also depends essentially on time (see Section C of this chapter), in all probability most of the effect described in Chapter 1 result from adsorption. However, it should be noted that the corrosion effect may appear under conditions of deformation at high rates if the contact time of the solid metal with the liquid metal preceding deformation is long.

On the basis of the considerations presented above concerning the mechanism of the corrosion influence of liquid metals, we can explain the experimentally observed regularities of the influence of various factors on the long term strength of materials.

In Chapter II, Section 2 we present the results of experiments characterizing the influence of temperature on the degree of corrosion damage to alloy EI827 in sodium and steel EI612 in lithium. They indicate that the long term strength reduction factor of the materials decreases continually with increasing temperature, that is the corrosion influence of the liquid metal increases. Since the values of coefficients at each temperature are determined for the same test duration, this regularity can be easily explained if we recall the exponential temperature dependence of the dissolution rate constant (see Part I, Chapter I, Section 1).

Figure 100 shows the results of investigation of the dependence of the influence of liquid sodium on EI869 alloy under conditions of constant load on the scaling factor. In this case, the effect is also fully determined by the corrosion influence of the medium - thermal mass transfer, since the alloy at this experimental temperature (750° C) showed no decrease in long term strength under isothermal static conditions. We can see from Figure 100 that the decrease in long term strength (time to rupture with constant load) is observed in a limited interval of specimen wall thicknesses.

The disappearance of the effect of corrosion by liquid sodium on specimens with low wall thickness (about 0.15 mm) is explained by the high rate of crack development and the relatively low rate of dissolution. Apparently, in this case the principle share of the time to rupture is occupied by the incubation period corresponding to the formation of cracks. The development of the latter can occur at high rates, since the wall thickness of the specimen is equal to the mean grain diameter of the alloy being investigated, so that an intercrystalline crack (this was the type of rupture observed) moves without encountering such serious obstacles as the joints between three grains.

The weakening of the corrosion effect of the liquid metal with increasing wall thickness of the specimen depends on the increase in crack length. Although as was noted in Part I, Chapter I, Section 1, the rate of dissolution of certain metals in sodium is determined by the rate of their transition through the interphase boundary, not by diffusion in the boundary film, in this case the determining effect was apparently diffusion. The layer of liquid metal in the narrow rupture crack can be looked upon as a local increase in the thickness of the boundary film.

We then come to the conclusion that an increase in crack length should lead to an increase in diffusion path of the metal dissolved in the end portion of the crack and, consequently, to a decrease in the rate of dissolution, and also to a decrease in the corrosion effect of the medium as a whole. Another factor which might be significant in the reduction in the rate of dissolution of the metal in the end portion of a long, narrow crack is the increased degree of "feeding" of the liquid metal solution in the crack due to dissolution of atoms from its walls.

The influence of the increased diffusion path on the scaling effect can be estimated as follows. On the basis of formula (7) the ratio of the maximum rate of dissolution of the metal (this value can be used due to the increased energy of atoms in the end portion of the crack) from shallow cracks c_1 and relatively long, deep crack c_2 will be $(dn/dt)_1/(dn/dt)_2 = c_2/c_1$. In the first approximation, considering the determining influence of the rate of corrosion on the rate of development of a crack, we can consider the $\bar{v}_1 \sim (dn/dt)_1$ and $\bar{v}_2 \sim (dn/dt)_2$, where \bar{v}_1 and \bar{v}_2 are the main rates of development of cracks in specimens with wall thicknesses δ_1 and δ_2 respectively. If we assume that c_1^* and c_2^* are the Griffith values of crack length in the specimens, then as above equation $(dn/dt)_1/(dn/dt)_2 = c_2^*/c_1^*$. Keeping in mind that $\bar{v}_1 = c_1^*/\tau_1$, $\bar{v}_2 = c_2^*/\tau_2$, and assuming that $c_2^*/c_1^* \approx \delta_2/\delta_1$, we produce $\tau_2/\tau_1 \approx (\delta_2/\delta_1)^2$.

Thus, the change in wall thickness of a specimen should have a strong influence on the effect of the liquid metal.

We can test the relationship produced using the data of the graph on Figure 100 b (its right portion). The quantity on the ordinate can be looked upon as values of time to rupture in relative units. Taking the extreme points $\delta_1 = 0.5$ mm and $\delta_2 = 2$ mm, we find $(\delta_2/\delta_1)^2 = 16$ and $\tau_2/\tau_1 \approx 7$, that is rather similar values. This result can be considered confirmation of the assumption of the action of the mechanism of influence of the medium described above. The somewhat weaker influence of the scaling factor produced in experiments in comparison to the calculated value is apparently determined by the lower rate of dissolution of the metal in the end portion of the crack and the maximum possible rate in these experiments [see equation (7)].

The determining influence of the ratio of the rate of crack development and the rate of corrosion is also indicated by the experimental data on duration of individual creep periods and plasticity during each period. It has been established that the changes in duration and relative elongation in the second and third periods in specimens tested in sodium with each value of wall thickness between 0.15 and 2 mm were of the same type as for the summary characteristics, that is the corresponding quantities in specimens tested in sodium were lower than in specimens tested in air. The relationship of these data to the concept outlined above concerning the influence of the corrosion of the material in a crack can be easily established if we consider the indication in the literature of the formation of cracks in metal at the beginning of the second creep period [400].

In Chapter II, Section 3 we find the results of experiments indicating a reinforcement of the corrosion effect of liquid bismuth on steel when the initial strength is increased. This effect results from the higher level of potential energy of atoms in the end portions of cracks (see Figure 142) in the high strength material than in materials of lower strength. The increase in the potential energy of atoms in turn should lead to an increase in the rate of their physical and chemical interaction with atoms of the medium, and there to an increase in the degree of influence of the medium.

The reinforcement of the corrosive effect of the liquid metal medium when its composition changes is a direct result of the increased content of the more active component. For example, an increase in the concentration of certain elements in the liquid metal melt may lead to an increase in solubility and rate of dissolution of the deformable metal or of some component in the case of an alloy. Quite similar effects are observed, as experiments have shown (see Chapter II, Sections 6 and 7) when the concentration of the active component in the solid metal is increased.

2. Mechanism of Facilitation of Plastic Deformation During Dissolution of Solid Metal in Liquid Metal

The facilitation of plastic deformation of a solid metal in a liquid metal medium is expressed as an increase in the creep rate under constant stress, and also as a decrease in the yield point and hardening factor during tensile tests at constant rate, is usually caused by the adsorption effect of the medium (see Section A, 1 of this chapter). In those cases when the liquid metal has only corrosion effect, the effects of facilitation of

plastic deformation have not been observed, with the exception of the trivial case of the reduction of the resistance to deformation with a significant decrease in the cross sectional area of the specimen carrying a load. We present below the results of a test of materials for creep in a medium of liquid sodium [415], which indicate an increase in creep rate under conditions of relatively weak corrosion influence of the medium.

Figure 144 shows the stable creep rate as a function of stress for EI869 alloy tested at 750° C in liquid sodium (under static and conduction conditions) and in air. The test method (see Chapter III, Section 1) assured that the process of thermal mass transfer of the material of the gauge section of the specimen occurred. We can see from Figure 144 that the creep rates of the alloy in air and in sodium under static conditions correspond, whereas in liquid sodium when mass transfer occurs the rate is noticeably higher, and the difference in creep rates increases with decreasing stress.

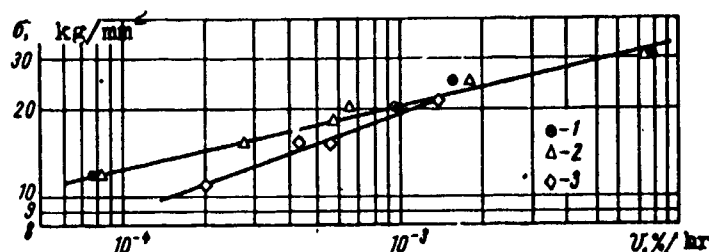


Figure 144. Stable creep rate as a function of stress for EI869 alloy at 750° C.
1 - tested in air; 2 - in sodium, isothermal static conditions; 3 - in convective sodium foil.

Figure 145 shows creep curves of two specimens of EI869 alloy at identical stress, 15 kg/mm². We can see that the specimen undergoing thermal mass transfer during the test shows a higher creep rate than the specimens tested in sodium under isothermal conditions, and that the increase in creep rate is observed not only during the second period, but during the first period as well. These regularities are not specific for EI869 alloy. They have also been observed in tests of other materials, for example, EI827 and EI765 alloys in liquid sodium, EI612 steel in liquid lithium.

The effect of increasing creep rate described above does not result from adsorption influences by the melted sodium, since under isothermal static conditions the sodium has no such influence on the material [4167]. This effect is also not related to the diffusion influence of the medium, since sodium does not diffuse into EI869 at 750° C, as spectral analysis has shown. The effect cannot be explained by a decrease in cross sectional area of the specimen as a result of corrosion, since special experiments studying mass transfer have shown (see Part I, Chapter II, Section 3) that the corrosion rate of EI869 alloy under these conditions is 0.02 mm/year. This means that even the specimen tested for 1000 hours would have a reduction in cross sectional area of less than 1%.

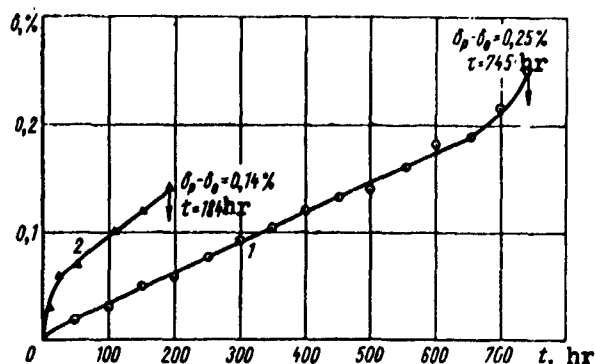


Figure 145. Creep curves of EI869 alloy under 15 kg/mm² stress at 750° C in medium of liquid sodium: 1 - tested under static isothermal conditions; 2 - in convective liquid metal flow.

The facilitation of plastic deformation of the metal in a corrosion active medium which dissolves the solid metal may occur due to various causes. This effect may be caused by the fact that as the corrosion front moves into the metal, dislocation sources which were previously "blocked" by various obstacles along the path of movement of the dislocations can become active again, as these obstacles are removed by corrosion. Some of the Frank-Reed dislocation sources with two points of attachment may be activated as a result of liberation of one point of attachment and movement of this end of the dislocation line to the surface, which has moved into the metal during the process of dissolution. The increase in the number of surface sources of dislocations with one point of attachment should also occur as a result of an increase in the surface of the metal as a result of corrosion. However, all of these processes can be effective only if the greater movement of the corrosion front is rather high.

The facilitation of plastic deformation described above apparently resulted from the following mechanism of the influence of the corrosion active medium. As was stated in Section A, 1 of this chapter, a dislocation which moves to the surface of the metal must overcome an energy barrier approximately equal to $b^2 \gamma$ [375]. Since there is a stress field around the dislocation, as it moves from the mass of the metal to the surface a highly stressed sector is produced before the dislocation. Obviously, the dissolution of metal atoms from the surface of this sector is more probable than from neighboring sectors. Thus, a dislocation or a part of a dislocation, may possibly be "dissolved," that is the atoms at the head of the dislocation may be dissolved into the liquid metal medium, so that the energy barrier ($b^2 \gamma$) no longer need be overcome. Schematically, the movement of the dislocation to the surface of the metal in an inert or liquid metal medium causes dissolution of the solid metal, as shown on Figure 146.

We present the following calculations to confirm the above. First of all, let us estimate the probability of dissolution of an atom at the center of a dislocation. The probability of dissolution on the atom from the nondeformed crystalline lattice is determined by the activation energy $Q_p = Q_0 + \alpha b^2 \gamma$:

$$W_p \sim e^{-\frac{Q_0 + \alpha b^2 \gamma}{kT}}, \quad (227)$$

where k is Boltzman's constant; T is the absolute temperature; α is a coefficient considering the mean increase in surface per atom upon dissolution. In the case of dissolution of an atom from the center of a dislocation (this is the area with the greatest distortion, and therefore has the greatest deformation energy density Q_d) the expenditure of energy required to dissolve an atom is Q_0 decreased by Q_d . Thus, the probability of dissolution of an atom from the core of a dislocation is characterized by the quantity

$$W_{pd} \sim e^{-\frac{Q_0 + \beta b^2 \gamma - Q_d}{kT}}. \quad (228)$$

Using expressions (227) and (228) and assuming $\alpha = \beta$, we find that the condition for appearance of the effect of facilitation of plastic deformation of the metal in the liquid metal medium dissolving the solid metal is

$$\frac{W_{pd}}{W_p} = e^{Q_d/kT} \gg 1. \quad (229)$$

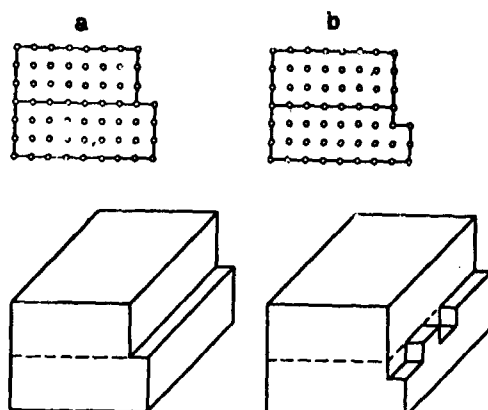


Figure 146. Diagram of displacement of edge dislocation to surface of metal deformed in inert (a) and liquid metal (b) medium, the latter causing dissolution of the solid metal.

Since the rate of dissolution is proportional to the probability of dissolution, conditions (229) can also be written in the form

$$\frac{v_{pd_0}}{v_p} e^{Q_{d_0}/kT} \gg 1. \quad (230)$$

Let us estimate the value of the ratio of dissolution rates v_{pd_0} / v_p . The approximate value of free energy of the core of the boundary dislocation, calculated for the atomic plane [376], is

$$Q_{d_0}^* \approx \frac{G a b^2}{3}, \quad (231)$$

where G is the shear modulus.

From this, the mean value of free energy of the atom at the core of the dislocation is

$$Q_{d_0} \approx \frac{G a^2 b^2}{3 \pi r_0^2}, \quad (232)$$

where r_0 is the radius of the core of the boundary dislocation.

Let us perform calculations for a nickel alloy, assuming $G = .7 \cdot 10^{-6} \text{ kg/cm}^2$ [260], $a = b = 3.5 \cdot 10^{-8} \text{ cm}$; $T = 10^3 \text{ }^\circ\text{K}$; r_0 will be determined from the assumption that there are 10 atoms at the core of the dislocation, from which $r_0 = 6.23 \cdot 10^{-8} \text{ cm}$.

Substituting these quantities into expressions (232) and (230), we find that the $v_{pd_0} / v_p \approx 1250$. Consequently, the rate of

dissolution of atoms at the core of a boundary dislocation is more than 3 orders higher than the rate of dissolution of atoms from neighboring, nondistorted sectors of the metal. Thus, the result produced can be looked upon as confirmation of the possibility of facilitation of plastic deformation of metal during the process of its dissolution.

Let us calculate the value of (230) for atoms at some distance from the center of the boundary dislocation. The expression for the mean deformation energy for one atom [376] in this case is

$$Q_d = \frac{Gab^2}{4\pi^2(1-\nu)(r_1^2 - r_0^2)} \left(\ln \frac{r_1}{r_0} - 1 \right), \quad (233)$$

where ν is the Poisson coefficient; r_1 is the radius of the area for which the deformation energy is being defined. Let us determine Q_d for $r_1 = 10^{-6}$ cm, using the same values of quantities in formula (233) which were used in preceding calculations; the Poisson coefficient will be considered equal to 0.3. Then we produce the value of $1.5 \cdot 10^{-15}$ erg/atom for the deformation energy density, and a value of $v_{pd}/v_p = 1.01$ for the ratio of the dissolution rates. Consequently, the rate of dissolution of atoms outside the core of the boundary dislocation is the same as for atoms of the undeformed metal.

We have now estimated the possibility of facilitation of plastic deformation due to dissolution from the energetic standpoint. We must also estimate the possibility of this process in consideration of its kinetics. Obviously, in this case the kinetic condition of possibility of facilitation of deformation consists of observation of inequality

$$t_p < t_d \quad (234)$$

where t_p is the time required for transition of an atom of a solid metal to solutions; t_d is the time required for the dislocation to move to the surface of the metal, that is for it to travel a path of length a .

We will consider the rate of dissolution to be approximately equal to the rate of diffusion of a dissolved atom in the non-moving boundary film of a liquid metal. Then the minimum distance equal to a , which the atom must travel in order to enter the liquid metal solution is determined by the expression

$$a \approx K \sqrt{D_{\chi} t_p}, \quad (235)$$

where D_λ is the diffusion coefficient of the dissolved metal in the liquid metal medium; K is a constant. Expression (235) yields the approximate value of the dissolution time.

$$t_p \approx \frac{a^2}{K^2 D_\lambda}. \quad (236)$$

Representing the rate of movement of the boundary dislocation as v_d and using equations (234) and (236), we produce the kinetic condition for possibility of facilitation of plastic deformation due to dissolution in the form

$$\frac{a}{v_d} > \frac{a^2}{K^2 D_\lambda} \quad (237)$$

and finally

$$v_d < \frac{K^2 D_\lambda}{a}. \quad (238)$$

We will consider $K = 2$, $a = 3.5 \cdot 10^{-8}$ cm. The values of diffusion coefficients in liquid metals [37] are usually $10^{-4} - 10^{-5}$ cm²/sec. Substituting these values into inequality (238), we find that $v_d < 10^3 - 10^4$ cm/sec.

In reference [417], the rates of movements of boundary dislocations in ferrosilicon are determined experimentally. It is established that in the temperature interval between 78 and 373° K, the rates of movement of dislocations vary between 10^{-6} and 10^{-2} cm/sec. The stress corresponding to the yield point in all cases corresponded to the rate of boundary dislocation movement of 10^{-3} cm/sec. Obviously, under conditions of material creep the rate of movement of dislocations will be even lower. Consequently the experimental data showed that a kinetic condition for the process in question (238) is also observed.

Thus, the estimates performed confirm the possibility of operation of the mechanism of facilitation of plastic deformation of metal in a corrosion active liquid metal medium. It should be noted that this mechanism is not specific for liquid metals, and can appear in any medium causing dissolution of the solid metal. It should also be noted that an increase in the rate of dissolution of the metal after its deformation has been repeatedly noted experimentally, and indirect confirmation of the possibility of this effect. Another confirmation of its possibility is the method of study of the process of deformation broadly used in laboratory practice, consisting of etching of metallographic sections. As we know, sectors with increased energy as a result of plastic deformation are etched preferentially.

It might be thought that the reason for the effective increasing creep rate is the formation of intercrystalline cracks in the metal which has been exposed to sodium in considerably larger numbers and with greater lengths than in the inert medium, leading to an increase in effective stress. However, this suggestion is negated by a comparison of the creep rate increase factors in the first and second periods. We see (Figure 147) that with constant stress the increase in creep rate is a result of the corrosion influence of sodium at the beginning of the process is greater than during its stable stage. This relationship of coefficients is explained similarly to the explanation presented in the discussion of the adsorption effect of facilitation of plastic deformation in section A, 1 of this chapter.

We should discuss the reason for the absence of the effect of increased creep rate in sodium under static isothermal conditions. Let us calculate time $t_{0.9}$ required to complete the process of dissolution under isothermal conditions to 90%. In Part I, Chapter 1, Section 4, it was stated that it is expressed by the formula $t_{0.9} = 2.3 V_L / S$, where V_L is the volume of the liquid metal; α is the dissolution rate constant; S is the surface of the solid metal from which dissolution occurs. For the specimens which we used, $V_L / S = 0.25$ cm. Since the literature contained no information on the value of α for nickel dissolved in sodium, we will perform our calculations using the dissolution constant of iron in sodium at 750°C : $\alpha = 4.53 \cdot 10^{-3}$ cm/sec [33], which is certainly no greater than the value of α for nickel. Using these quantities, we find that $t_{0.9} = 2$ min.

Since heating of the specimen on the long term strength testing machine is performed rather slowly, and since two hours generally pass after the required temperature is reached before the load is applied to the specimen, these two hours being used for precise adjustment of the temperature, it is quite obvious that deformation of the specimen under isothermal conditions begins with the process of dissolution in the practically saturated liquid metal solution complete.

Chapter III, Section 2 presented experimental data on the influence of temperature on the effect of facilitation of plastic deformation (creep) of EI827 alloy in liquid sodium. The regularity produced (see Figure 110) - an increase in the effect of an increasing temperature - is explained by the increase in the rate of the process of dissolution.

Data on the influence of the scaling factor (see Chapter III, Section 3) can be explained by the fact that with a significant decrease in wall thickness of the specimen and increase in

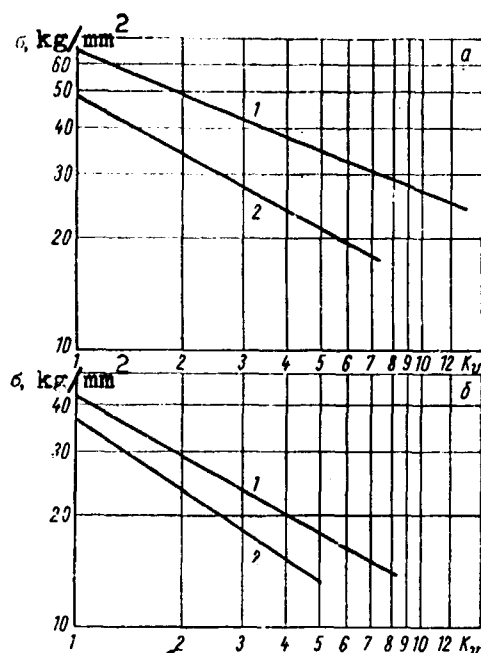


Figure 147. Mean creep rate increase factor in the first period (1) and stable creep rate (2) as functions of stress for EI827 (a) and EI765 (b) alloys at 750° C in liquid sodium under thermal mass transfer conditions.

deformation rate, condition (238) is not fulfilled and the effect disappears. An increase in wall thickness of the specimen and the corresponding "polycrystallinity" leads to a weakening of the role of surface effects in the deformation process, which also results in disappearance of the effect at a certain value of the ratio of mean grain diameter to wall thickness (in experiments with EI869 alloy, $d/\delta \approx 0.15$).

In conclusion, we must emphasize that, in spite of the facilitation of plastic deformation of the material when it is dissolved in a liquid metal medium, the total elongation of specimens at rupture is less than in an inert medium. This is a result of the fact of accelerated crack growth under the influence of the liquid metal, as was pointed out in the preceding section.

3. Influence of Oxygen in Purity in Sodium on Long Term Strength of Materials

In Chapters VI, Part I of this book we indicated that the corrosion influence of liquid sodium on unstressed materials is increased as a result of contamination of the sodium with oxygen. Correspondingly, we should expect a worsening of the strength properties of materials in contact with sodium containing increased quantities of oxygen.

Tests were performed for long term strength of EI869 alloy in sodium with various oxygen contents at 750°C [276]. Tubular specimens were tested with wall thicknesses of 0.5 mm and internal diameters of 10 mm. Pure sodium, containing about 0.01 weight % O_2 was produced by filtration using a special device. High oxygen contents (1 and 10% of the weight of the sodium in the internal cavity of the specimen) were achieved by introducing the required quantity of sodium peroxide to the specimen before welding on the plug; sodium peroxide, as we know [135], decomposes at high temperature to sodium oxide and oxygen. The long term strength tests were performed with monoaxial extension of the specimens according to the normal method. In addition to the sodium-containing specimens, control specimens were generally tested, with the internal cavities filled with argon.

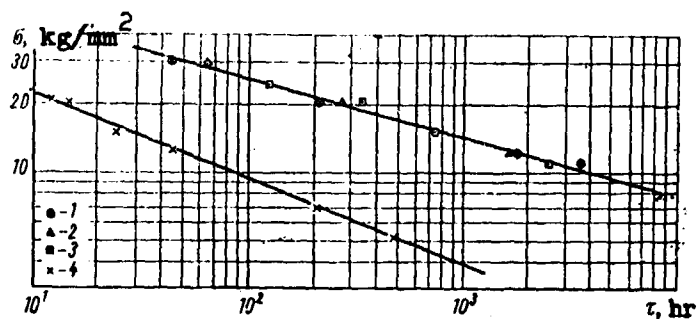


Figure 148. Time to rupture as a function of stress for EI869 alloy in air and in sodium under static conditions at 750°C :
1 - tested in air; 2 - in sodium with 0.01 wt % O_2 ; 3 - in sodium with 1 wt % O_2 ; 4 - in sodium with 10 wt % O_2 .

Figure 148 shows the diagram of the long term strength of EI869 alloy. We can see that the alloy has an identical long term strength in air and in pure sodium. The long term strength of the

alloy is also unaffected by the introduction of 1 wt % O_2 to the liquid sodium. Increasing the content of the oxygen impurity to 10 wt % causes a sharp drop in long term strength of the material: the degree of decrease in strength with this contamination of sodium is equivalent to that caused by increasing the temperature by approximately $100^\circ C$. The construction of creep curves showed the absence of any influence of pure sodium and sodium containing 1 wt % O_2 on the creep rate of EI869 alloy. In sodium with 10 wt % O_2 , the creep curves were changed so sharply that the ordinary three periods can not be separated on them; some specimens in sodium with 10 wt % O_2 showed negative creep. All of these changes are a result of the chemical interaction of the alloy with the oxygen in the sodium.

Microscopic analysis of rupture specimens has shown that pure sodium causes no structural changes in the alloy (Figure 149). In specimens tested in sodium strongly contaminated with oxygen the internal surface showed a layer of products of the interaction of the alloy with sodium oxide. Inspection of metallographic sections also clearly shows an increase in the number of inter-crystalline cracks and the depth of their penetration into the structure of the metal.

Regularities of the influence of an oxygen impurity in sodium on long term strength of materials similar to that described above were also observed in the testing of alloy EI765 [276]. A decrease in long term strength as a result of contamination of sodium with oxygen was also noted for EI851 steel [282], although in this case a slight effect was observed at a concentration of 1 wt % O_2 .

If we compare the data of tests in sodium with 1 and 10 wt % O_2 , we notice the absence of any influence of sodium with 1 wt % O_2 on EI869 alloy, compared to the strong influence of sodium with 10 wt % O_2 . Although different quantities of oxygen were placed in the internal cavity of the specimens, since in both cases it exceeded the equilibrium concentration (0.38 wt % O_2 [136] at the experimental temperature of $750^\circ C$), liquid metal of the same composition was in contact with the gauge section of the specimens; the excess quantity of sodium oxide was present as a second phase. This indicates that the mechanism of the effect of the liquid metal on the material of the specimen, as well as the intensity of the process in the two series of experiments should have been the same. The difference in the effects of the medium on the long term strength of the alloy produced in spite of the identity of the mechanisms is apparently explained by the difference in the

absolute oxygen content in the system. Actually, metallographic analysis of specimens ruptured in sodium containing 10% O_2 and analysis of the creep curves indicate that the earlier rupture was caused by the corrosive influence of the medium - chemical interaction of the material of the specimen with the sodium oxide. The degree of damage in this case depends on the portion of the cross section of the specimen subjected to corrosion which in turn depends on the quantity of the reagent in the system and the dimensions of the cross section. Therefore, the following corrosiveness factor can be used to characterize the corrosiveness of the oxygen in the liquid metal system:

$$K_{cor} = \frac{P_{O_2}}{S \delta_{min}}, \quad (239)$$

where P_{O_2} is the weight of oxygen in the system; S is the area of the entire surface of the structural material in contact with the liquid metal; δ_{min} is the minimal transverse dimension of the submerged portion of the specimen (wall thickness in the case of a tubular specimen).

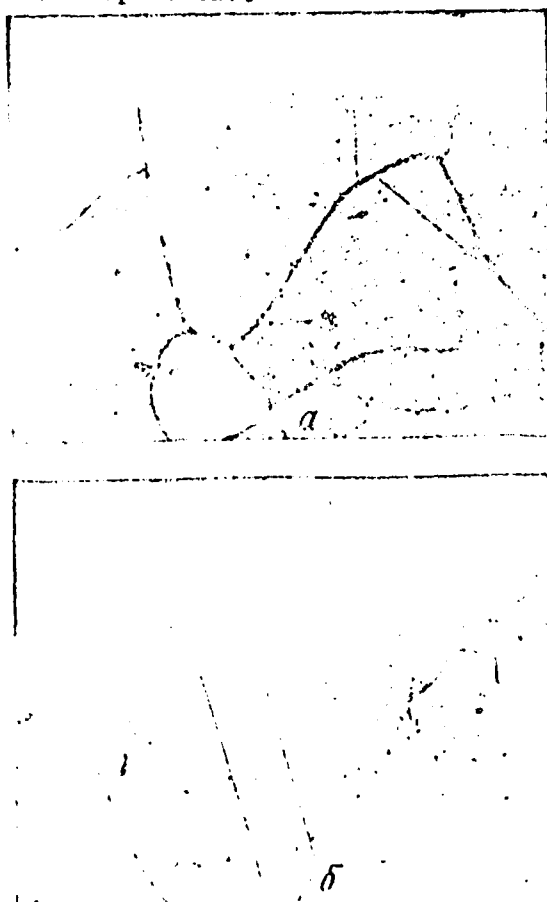


Figure 149. Microstructure of surface layer of EI869 specimens after long term strength testing at 750° C (by 150):
a - tested in sodium with 0.01 wt % O_2 , $\sigma = 12 \text{ kg/mm}^2$, $\tau = 1885 \text{ hr}$; b - in sodium with 10 wt % O_2 , $\sigma = 5 \text{ kg/mm}^2$, $\tau = 487 \text{ hr}$.

For long term strength tests in sodium of 10 wt % O_2 in the experiments described above, the corrosiveness factor was 4.9 g/cm^3 , while for tests with 1 wt % O_2 it was about 0.5 g/cm^3 .

As the experimental data show, no influence of oxygen on the long term strength of a nickel alloy at 750°C in a static sodium system should be expected if the corrosiveness factor is less than 0.5 g/cm^3 . However, type EI851 chrome-nickel austenitic steel does experience some influence of sodium at 700°C even where $K_{\text{cor}} = 0.5 \text{ g/cm}^3$ [282]. The performance of experiments on the determination of long term strength of various materials in sodium contaminated with oxygen should provide the critical values of corrosiveness factor for materials of various classes.

In connection with these results, we must also note that although quite high per cent contents of oxygen in sodium were used in order to produce the effect of decreased long term strength, this does not mean that the influence of oxygen in any liquid metals system will be observed only at these high degrees of contamination. We know that large sodium installations are carefully screened and the content of oxygen in them is maintained at low levels. However, since the effect of the influence is determined by the absolute content of oxygen in the sodium, even with high purification but with a large ratio of the volume of liquid metal to the area of the internal surface of the installation, the aggressiveness factor of the oxygen may be rather high. Of course, we must recall the existence of the lower boundary of the effect - the minimum concentration of oxygen in the sodium at which the chemical reaction can occur.

4. Influence of Electrotransfer on Long Term Strength of Materials in Sodium

Earlier, we presented the results of tests of the alloys EI869, EI827 and EI765 for long term strength in sodium under thermal mass transfer conditions. It was demonstrated that the decrease in the long term strength results only from the corrosion influence of the medium. Careful studies of mass transfer have been established that an electromotive force arises between the ends of a long term strength specimen under tensile stress (see Figure 95). It has been determined in exactly the same manner as the EMF of convection chambers is determined (see Part I, Chapter VII). Electrodes of KH18M10T steel were welded to the upper end of an extension tube made of KH18M10T steel and to the specimen beneath its gauge portion. Consequently, one end of the upper electrode was at the temperature of the cold zone of the liquid metal system, on the other end was at room tempera-

ture; the ends of the second electrode were at the temperature of the hot zone and at room temperature. Connection of a potentiometer to these electrodes demonstrated that an electromotive force arises between the ends of the specimen, related to the presence of a liquid metal inside the specimen. The correctness of this conclusion is confirmed by the fact that the EMF is several millivolts when the liquid metal is present in the specimen and the temperature difference between the hot and cold zones is several hundred degrees, and only 0.1-0.2 mv when the liquid metal is absent in the specimen with the same temperature difference.

The electromotive force produced is thermoelectric, not electrochemical in nature (see Part I, Chapter VII). However, there is reason to believe that it might influence the corrosion process even in this case.

Weeks and Klamut, as was stated earlier, assume [62] that the high electrical conductivity of liquid metals under the influence of a thermal electromotive force might result in the formation of a powerful electric current, causing electrotransfer of components of structural material. Therefore, we must determine whether the reduction in long term strength of the material is related to the electromotive force and consequently to electrotransfer, or whether the corrosion process is determined only by thermal mass transfer.* Tests of long term strength under conditions of mass transfer with the passage of a constant electrical current through specimens were performed for this purpose [419].

A diagram of the experiment is shown on Figure 150. The DC source used was a selenium rectifier type VSG-3M. The current in the specimen circuit was regulated by a rheostat, with the required current established at the beginning of the experiment then left constant right up to the moment of rupture of the specimen. Type EI869 alloy was used in the test. The temperature of the gauge portion of the specimen was 750° C, the temperature of the cold zone - about 400° C. These temperature conditions were maintained during testing of the specimens with and without current. In all tests, the current was maintained at 190 A. The specimens were tested for long term strength at a stress of 15 kg/mm². The tests were performed using types UIM-5 machines. The results of the tests are presented in Table 54.

* In these long term strength tests, in contrast to the corrosion tests, the electric circuit through the convection chamber was closed through the support of the machine and a current passed through the circuit.

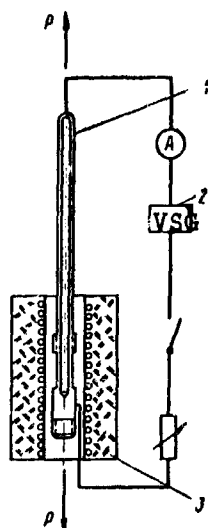


Figure 150. Diagram of tests of specimens for long term strength in liquid metal under thermal mass transfer conditions with electric current from external source passing through specimen: 1 - specimen; 2 - rectifier; 3 - electric furnace.

Table 54

Results of Tests of EI869 Alloy for Long Term Strength in Sodium at 750° C at 15 kg/mm² Load with Electric Current Passing Through Specimen

Current, a	Polarity (sign) of specimen	Time to rupture, hr	Deformation creep (elongation), %
-	No current	161	0.20
-	" "	197	0.24
-	" "	97	0.19
190	-	124	0.21
190	-	115	0.22
190	+	202	0.18
190	+	131	0.13
190	+	146	0.49
-		1639*	0.82*
* Specimen tested in air			

As we can see from the table, the liquid sodium causes identical reduction in long term strength of the material in comparison with this level in air, regardless of whether an electric current passes through the liquid metal medium or not. The direction of the electric current in the liquid metal medium also has no effect on the long term strength of the material. The values of time to rupture of all specimens in sodium lie within the limits of normal variation for long term strength tests.

We mentioned above that a current of 190 a passed through the circuit. Of greatest interest is the electric current and intensity in the liquid metal flow. Considering that the tube and the liquid metal which fill it form a circuit consisting of parallel connected conductors, we can determine that the current passing through the liquid sodium was approximately 160 a, through the tube - 30 a. The current density through the sodium was 204 a/cm^2 , that is rather high.

In a moving liquid metal medium, of course, we cannot observe the same effects of the electrotransfer of dissolved elements as observed under static conditions in experiments with capillary tubes [418, 420]. However, we can assume that the additional impetus imparted to the atoms in solution under the influence of the electrical current will either lead or hinder their movement under the influence of convection forces toward the upper, cold portion of the chamber. Consequently, if the impetus was high enough, it could influence the process of mass transfer, accelerating or retarding it.

Naturally, the influence of an electrical current should depend on its direction. Whereas with one direction with current the movement of the ions in the liquid metal solution toward the cold zone will be more rapid, when the polarity is changed the movement of the ions should be retarded by the effect of the current. It is interesting to note that in the ascending and descending flows of liquid metal the electrical impulses act on the ions in the same direction, but in the ascending flow they accelerate or decelerate the movement of the ions to the cold zone (zone of crystallization) while in the descending flow they correspondingly retard or accelerate the movement of the same ions toward the hot zone (dissolution zone). Consequently, when tests are performed using the method described above, the electric currents should accelerate or retard while mass transfer, acting on both of the liquid metal flows.

In the considerations outlined above show how an electrical current can influence the process of thermal mass transfer. The electric current may result from a thermoelectromotive force

arising between the ends of a specimen or from an external source. In experiments on the long term strength of EI869 alloy in liquid sodium, the thermoelectromotive force amounted to a few millivolts. Consequently, it was necessary that the external source of current create a potential difference between the ends of the specimen at least no less than the thermoelectromotive force. Only when this condition can be observed can the electrical current caused by the external source (if the direction is opposite) overcome the influence of the thermo current in mass transfer, if the thermo current has such an influence. In the experiments described above, the potential difference resulted from the external source exceeded the thermoelectromotive force by approximately one order of magnitude. Consequently, the condition necessary for such tests was observed. In spite of this, as the experimental results show, the electric current had no influence on either the time to rupture of the specimens or their plasticity.

Thus, we can conclude that the electric current caused by the thermoelectromotive force has no influence on the process of thermal mass transfer of EI869 alloy in liquid sodium, which leads to early rupture of specimens in comparison with tests in air. The influence of the liquid metal medium is neither increased nor decreased with an electric current density considerably higher (approximately one order of magnitude), achieved by connection of an external DC source to the liquid metal system.

C. Diffusion Influence

The diffusion influence of a liquid metal, in contrast to the adsorption influence, occurs not at the phase boundary, but rather within the structure of the metal deformed, and leads to changes in the mechanical properties of a certain sector of the metal. Thus, the diffusion influence is not a surface influence, but rather a volumetric influence. Diffusion of atoms of the liquid metal into the solid metal forms a layer of solid solution. Consequently, the nature of the influence of the medium depends on the mechanical properties of the solution. Another essential difference between the diffusion influence and the adsorption influence is that the former is irreversible, while the latter is reversible.

Changes in the mechanical properties during dissolution can seemingly be determined on the basis of practice of alloying of metals. However, alloying results in an increase in strength and yield point and an increase in creep resistance of alloys, that is the influence of alloying is opposite to that of liquid metals (in certain cases the nature of the influence of liquid metals and alloying may be the same; for example, see the results of tests of monocrystals for creep [279]).

The mechanisms of the increase in strength of solid solutions in comparison to pure metals may be various: interaction of the stress field around atoms of the alloying elements with the stress field of moving dislocations; inhibition of extended dislocations; formation of close order; precipitation of dissolved atoms on dislocation steps and resulting impediments to motion; chemical interactions of atoms of the alloying element and atoms of the base metal, etc. [376, 393, 421-424]. Obviously, the influence of these mechanisms in alloying of any element will be the same: an increase in the strength of the solid solution. Therefore, the weakening influence of the liquid metal diffusion into the solid metal must not be related to these mechanisms.

We must emphasize that the practice of alloying involves primarily introduction of high-melting elements to metals. This generally leads to an increase in the bonding forces in the crystalline lattice [425 - 427]. One essential difference in the alloying of low-melting elements is apparently the lower values of bonding forces between the different atoms than between the atoms of the base metal. This influence of alloying is indicated by the decrease in the melting point of the solid solution. Obviously, the influence of this factor, causing a decrease in strength, will in some cases be greater than the influence of the changes in lattice parameter resulting from differences in the atomic radii of the dissolved metal and the solvent. Furthermore, there is an indication that distortion of the crystalline lattice is an unfavorable factor for long term operation of a metal at high temperature, for its heat resistance and should be kept to a minimum [423]. The diffusion influence of a liquid metal medium at high temperature, leading to a decrease in long term strength and an increase in creep rate, may be a result of the decrease in activation energy of self diffusion of the base metal due to distortion of its lattice.

Formation of solid solutions with high concentrations of the metal of the medium are highly possible in the practice of the usage of structural materials in liquid metal media. Therefore, there is greater interest in cases of very low solubility of the liquid metal in the solid metal. Although the degree of the influence of the dissolved metal on the bonding forces, melting point of the solution, etc., increases with increasing concentration, an essential decrease in the strength and plasticity of the solid metal is possible even with a negligible amount of the low-melting metal present. This influence is most probable if the dissolved element is homophilic. In this case, it might be expected that an increase in its content at the grain boundaries would lead to a decrease in the coefficient of viscosity at high temperature which, in turn, causes an increase in the creep rate due to the increased share of intercrystallite slipping, and also

leads to earlier formation of intercrystallite cracks and rupture than in an inert medium. The horophilicity of atoms of the liquid metal can facilitate rupture of a solid solution not only along grain boundaries, but along boundaries of mosaic units, along slipping planes and along sectors of "pretransient" type structures in aged alloys if subcrystalline internal adsorption occurs [428-430].

The case of the influence of a small impurity of a horophilic metal on the metal being deformed which we are analyzing results from the diffusion influence of the medium, but it is still a mixed diffusion-adsorption influence. The reason is that the accumulation of the low-melting metal along the grain boundaries leads to a decrease in their free surface energy. However, in spite of this the adsorption influence of the horophilic metal and the ordinary adsorption influence resulting from processes of interaction on the boundary between the solid and liquid metals differ essentially. First of all, the degree of decrease of surface energy of the metal at the boundary with the liquid phase is greater than that which results from the presence of a small amount of the low-melting metal in the boundary zone or surface layer. Secondly, rupture in the case of "phase adsorption" begins at the surface, while in the case of the influence of the horophilic impurity it begins in the volume of the metal. Third, the magnitude of the adsorption effect with "phase adsorption" depends on the rate of propagation of a crack and the rate of penetration of liquid metal in the crack; the presence of the horophilic impurity along the grain boundaries excluded influence of these kinetic factors for the beginning of deformation, and the magnitude of the effect is determined by the deposition density of impurities in the boundary zone of the metal deformed. Fourth, the adsorption effect in the case of "phase adsorption" is reversible, while the similar effect caused by horophilic impurities is irreversible. Since the influence of horophilic impurities is possible only after diffusion has occurred, that is it results in the final analysis from the occurrence of diffusion, this mixed form of influence of the liquid metal medium should be analyzed in the section on diffusion influences.

Regardless of whether the low-melting metal diffuses evenly through the volume of the solid, deformed metal or principally along grain boundaries, the influence of the medium on the development on rupture cracks can be represented as follows. The diffusion of atoms of a medium leads to a change in the physical mechanical properties of the damaged sector of the solid metal (Figure 151). Since the zone of plastic deformation of the metal is located near the end portion of the crack, and since the diffusion is accelerated due to the plastic deformation [431-434], the diffusion front here penetrates somewhat more deeply into the

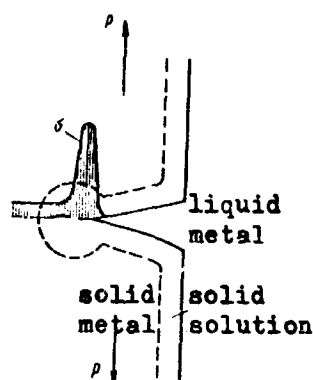


Figure 151. Diagram of rupture of metal in diffusion active liquid metal medium. (P - load; σ - stress).

metal than at neighboring sectors. Penetration of the crack into the depth of the specimen now requires breaking of bonds between atoms which are components of the solid solution. Since the bond forces in the solid solution, one component of which is the low-melting metal, are weaker than in the initial pure metal, they are broken with a lower value of applied stress in the case of tests with constant deformation rate, or breaking of the bonds requires a lower degree of thermal fluctuations in the case of tests with constant stress. In fatigue tests, the movement of a crack occurs with a lower value of plastic deformation of the metal adjacent to the end portion of the crack, or with a lower concentration of vacancies [370, 435, 436] than when the diffusion effect of the medium is absent.

In tensile tests with constant rate of deformation, the diffusion effect of the medium in a crack can be characterized by a certain mean value of specific work φ over the length of the crack. Then the change in energy of the metal during the formation of a crack of length c is expressed in the form

$$\Delta E = 2\gamma c + \mu c - \varphi c - \frac{\sigma^2 c^2}{2E_\varphi}, \quad (240)$$

where E_φ is the local value of modulus of elasticity of the metal in the diffusion zone; the remaining symbols are the same as in formula (180). Using equation (240) and the condition for the formation of a Griffith crack $d\Delta E/dt = 0$, we produce the following expression for the rupture resistance

$$\sigma_R = \mu \sqrt{\frac{E_\varphi (\gamma + \mu/2 - \varphi/2)}{c}}. \quad (241)$$

Thus, the greater the weakening the bonding forces in the diffusion zone, the greater the equivalent work φ , the greater the decrease in strength of the metal.

The dynamic effect is apparently significant in the diffusion influence of the medium, in addition to the static effect of weakening of bonds in the lattice of the metal, which is also present if the solid solution is formed for the beginning of the test. Its influence is related to continuous diffusion of the atoms of the medium during deformation of the metal. The movement of the diffusion flow of atoms apparently can lead to a decrease in stability of the atoms which are in the metastable position in the crystalline lattice. Under the influence of the diffusing atoms of the medium, the atoms of the base metal will receive additional impetus, which facilitate their transition to a more stable position. Apparently, this influence can lead to liberation of the inhibited boundary dislocation, to creep of this dislocation to neighboring slipping planes as a result of transition to a new position of atoms at the edge of the dislocation plane. Apparently, the additional impetus of the diffusion atoms also facilitates rupture of the bonds between atoms in the end portion of the crack when the metal is tested for long term strength, since this impetus decreases the thermal fluctuations supporting rupture of the bonds.

The diffusion influence of the liquid metal may be particularly greatly increased with unstable temperature regime of deformation if the temperature dependence of the solubility of the liquid metal and the solid metal is sharply expressed. In this case when the temperature is decreased the second phase may separate; liquid metal, intermetallic compound or super saturated solution, which looses coherent coupling to the initial solid solution. Naturally, the most dangerous effect is the separation of the liquid metal, since sectors of the new phase in this case forms seeds for rupture cracks.

One essential feature of the effect of the diffusion influence of liquid metal on solid metal is its time dependence. The longer the contact between the liquid metal and the solid metal before or during deformation, the greater the depth into the specimen which the diffusion front can move, the greater the change in the mechanical properties of the metal being tested. Table 55 shows the dependence of mechanical properties of lead specimens in extension at constant rate, as well as the number of bends on contact time with mercury before the beginning of the experiment [437]. The tests were performed using flat specimens with a gauge section thickness of 1.2 mm and a width of 5 mm. We can see from the table that as the duration of contact of specimens with mercury increases, the effect (decrease in strength, plasticity and number of bends) of the contact increases continually. The decrease in the degree of change of mechanical properties as contact time increases it apparently caused by the approximation of the solid solution concentration to the equilibrium of level.

The considerable solubility of mercury in lead is confirmed by the data of [119].

An influence of holding time in liquid metal on the mechanical properties of a solid metal similar to that described above was also observed in short term tensile tests of type L62 brass [438] and copper-beryllium [237] after contact with mercury.

The following observation, made during tests of armco iron for creep in liquid zinc, saturated with iron (see beginning of this chapter) is also related to the influence of time on the diffusion effect of the liquid metal: the degree of influence of the liquid metal on the creep rate of armco iron in the second period was greater than the first period, that is the value of the creep rate increase factor for the second period was greater than for the first, with all values of applied stress (Figure 152). This fact as well as the increase of the effect with decreasing stress, are determined by the more complete occurrence of diffusion processes as the diffusion time of atoms of the medium into the deformed metal increases. We must note here that the relationship between creep rate increase factors with adsorption and corrosion by the liquid metal (see Sections A and B of this chapter) and with the diffusion effect differ.

Table 55

Mechanical Properties of Type S3 Lead
Specimens has a Function of Contact
Time with Mercury before the beginning
of the Test

Time of exposure to mercury, sec	σ_B , kg/mm ²	S_k , kg/mm ²	δ , %	ψ , %	Number of bends
0	13.1	89.2	62	84	15
60	12.9	51.0	57	74	14
600	11.4	19.1	57	46	3
1800	10.5	14.8	57	30	2
3600	10.5	14.7	57	25	1
7200	10.4	12.6	56	17	1

The decrease in strength and plasticity of monocrystals under the influence of a liquid metal coating is also sometimes related to volumetric diffusion of atoms of the medium, as was shown by the works of V. N. Rozhanskiy [439, 440]. The diffusion of liquid metal, as these works indicate, sometimes leads to the formation of new phases, to the rupture of specimens along planes of induced cleavage. Works on the investigation of internal friction in metal specimens with thin surface coatings of low-melting metal also indicate the diffusion influence of liquid metals [280, 281, 441]. The increase in internal friction established in these works is proportional to the increase in grain boundary surface area, indicating intercrystalline diffusion and homophilicity of the diffusing metal.

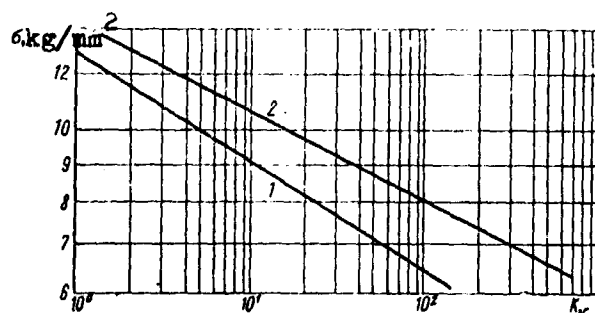


Figure 152. Creep rate increase factor in the first (1) and second (2) periods has a function of stress in tests of armco iron in liquid zinc saturated with iron at 500° C.

An indirect indication of the possibility of reducing the long term strength of materials as a result of the diffusion of low melting metals can be found in the results of [442-444]. These works showed that the time to rupture at relative elongation of heat resistant alloys tested under constant stress at high temperature decrease sharply even with negligible contents of Pb, Sb, Bi and other low melting metals. For example, in the Fridantsev established reference [443] that the time to rupture for specimens of type EI437 nickel alloy at 700° C with a stress of 36 kg/mm² is 88, 28 and 12 hr with a content of lead in the alloy of 0.0006, 0.0015 and 0.0050 wt. % respectively.

Since appearance of the diffusion influence of the liquid metal on the solid metal during the deformation process requires more rapid movement of the diffusion front into the depth of the specimen than the movement of a crack, there is a kinetic condition for the diffusion effect. In the case of tensile testing

of a metal at constant deformation rate, this condition can be produced as follows. We represent by t_0 the time to rupture of a specimen stretched at rate $\dot{\epsilon}$ in an inactive medium. Suppose its elongation at the moment of rupture is δ ; then $t_0 = \delta / \dot{\epsilon}$. We represent by t_1 the time required for diffusion penetration of the liquid metal through a layer of the metal of the specimen with thickness equal to its diameter L . If the diffusion factor (volumetric or boundary, depending on the nature of propagation of the crack) is D , then $t_1 \approx D/L^2$. Since facilitation of crack development is necessary for fulfillment of inequality $t_1 < t_0$, the kinetic condition for appearance of the diffusion effect of the liquid metal will be

$$\dot{\epsilon} < \frac{D\delta}{L^2}. \quad (242)$$

Thus, the diffusion influence of the medium can appear only with specimen deformation rates for which inequality (242) is fulfilled. At higher rates of deformation, the specimen will not experience the diffusion influence of the liquid metal. However, it should be noted that condition (242) is correct if the contact time of the specimen with the liquid metal before the test is not great, that is if it is much less than t_1 .

It was shown in Chapters II and III that the diffusion influence of the liquid metal on the long term strength and creep of materials increases with decreasing temperature. For example, tests at constant stress have shown that the relative decrease in time to rupture and increase in stable creep rate of armco iron under the influence of liquid zinc are greater, the lower the temperature (see Figure 96, b and 109, b). The results of these tests seem at first glance to be paradoxical, since the diffusion factor increases exponentially with increasing temperature. However, this influence of the diffusion factor of the liquid metal is quite normal. During long term strength tests, it is possible if the activation energy for diffusion of the liquid metal in the solid metal is less than the activation energy for rupture of the solid metal. This can be demonstrated as follows.

The diffusion influence of the liquid metal on a specimen at two different experimental temperatures is approximately the same if the depth of the diffusion zone is equal. Let us represent by l_1 and l_2 the depths of diffusion penetration of atoms of the medium into the specimen at temperatures T_1 and T_2 ($T_2 > T_1$). If

the diffusion is volumetric, then $\ell_1 = K\sqrt{D\tau_1}$ and $\ell_2 = K\sqrt{D\tau_2}$. we will assume that τ_1 and τ_2 are the values of time to rupture of specimens at temperatures T_1 and T_2 respectively. Having in mind the relationship $\tau = B e^{Q/RT}$, where Q is the rupture activation energy, and since $D = D_0 e^{-Q_D/RT}$, where Q_D is the diffusion activation energy of the liquid metal into the solid metal we produce

$$l_1 = KD_0^{1/2} \exp \left[\frac{1}{2RT_1} (Q - Q_D) \right]$$

and

$$l_2 = KD_0^{1/2} \exp \left[\frac{1}{2RT_2} (Q - Q_D) \right]. \quad (243)$$

Obviously, the degree of diffusion influence of the medium is determined by the ratio ℓ_1/ℓ_2 , which is equal to

$$\frac{l_1}{l_2} = e^{\frac{1}{2R} (Q - Q_D) \left(\frac{1}{T_1} - \frac{1}{T_2} \right)}. \quad (244)$$

If $\ell_1/\ell_2 = 1$, the degree of influence of the liquid metal at various temperatures will be the same. We can see from equation (244) that this case is possible if the activation energies for rupture and diffusion are the same. If $\ell_1/\ell_2 > 1$, when the temperature is decreased the effect of the influence of the medium increases. It follows from (244) that this is possible if the rupture activation energy is greater than the diffusion activation energy. Finally, if $\ell_1/\ell_2 < 1$, the degree of influence of the liquid metal increases with increasing temperature. This last case is possible if the rupture activation energy is less than the diffusion activation energy.

Since the value of Q_D included in equation (244) represents the diffusion activation energy in the metal near the end portion of a crack with strongly distorted structure as a result of the plastic deformation which has occurred, its value should be rather low. In any case, it should be not over the activation energy for surface diffusion which, according to the calculations of S. T. Kishkin [445], might be approximately 10 kcal/g.atom. The value of rupture activation energy is generally several tens of kcal/g. atom. Therefore, in most cases the second of the variants analyzed above is realized when a liquid metal diffuses into a solid metal.

Commonality and Diffusion of Adsorption, Corrosion and Diffusion Factors

The effects of the influence of liquid metals on solid metals in the stressed state described in the second portion of this book result from the effects of the adsorption, corrosion and diffusion factors. The macro effect observed experimentally is a result of the individual or combined influence of these factors.

Experimental investigations have indicated that all three factors act in the same direction and lead to a decrease in the strength and plasticity of the solid metal, or in certain cases made plasticize it. The effects of each of these three factors are thermal dynamically determined, since the solid-liquid metal system is brought to a state with lower thermal dynamic potential than its potential in the initial state.

The identical nature of the influence of the adsorption, corrosion and diffusion factors on the mechanical properties of the metal deformed is based on the identical nature of their influence on the atomic bonding forces in the solid metal, namely a weakening of the atomic bonds. The mechanism of the influence of the liquid metal medium on the strength and plasticity of the solid metal in the limiting cases, when only one of the three factors has an influence, can be conveniently analyzed by using the diagrams of the interaction of the atoms of the medium and the solid metal in the end portion of a crack (Figure 153). The stability of the crack in the field of external forces results from the bonding forces of atoms in its end portion. It can be considered approximately that it is determined by the bonding force f_{AA}^0 of the pair of atoms A - A whose interaction energy is maximal (see Chapter V, A, 1).

The penetration of atoms of an adsorption active liquid metal into the crack leads to weakening of bonding force f_{AA}^0 to the value f_{AA} and to the establishment of new bonds f_{AB} (see Figure 153, a). At this point, the crack can propagate by one interatomic distance by breaking bonds f_{AA} and f_{AB} , not bond f_{AA}^0

as before. Therefore, the condition of the adsorption influence of the medium is written in the form

$$f_{AB}^y + f_{AA}^y < f_{AA}^0, \quad (245)$$

where the superscript y indicates that the corresponding values are projections of vectors on the y axis, corresponding to the direction of the influence of the external medium.

Due to the capability of adsorption active medium atoms to perform surface migration, one atom of the medium is in principle sufficient for propagation of a crack through the entire cross section of the solid metal (having in mind a flat model one atom thick).

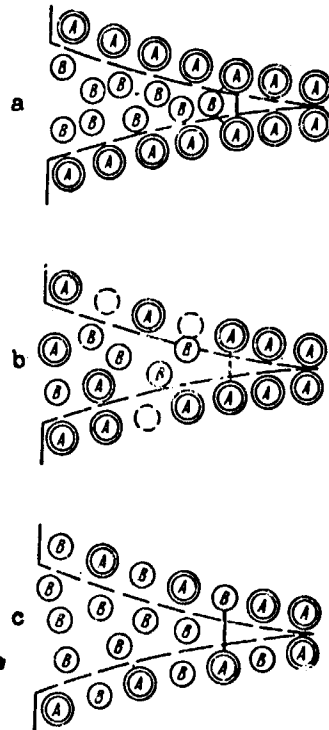


Figure 153. Diagram of adsorption (a), corrosion (b) and diffusion (c) influences of liquid metal on solid metal at end portions of crack.

One specific feature of the adsorption influence is its reversibility: after the medium is removed, the mechanical properties of the metal become the same as in the initial state.

The corrosive influence of the liquid metal, related to the dissolution of solid metal - the most frequently encountered form of corrosive destruction - causes breaking of the bonds of two light atoms A - A in the end portion of the crack as well. This rupture is facilitated by the transition of one atom into the liquid metal solution (see Figure 153, b). Thus, the condition for the corrosive influence of the medium is written as follows:

$$f_{AA}'' < f_{AA}''^0. \quad (246)$$

Obviously, the effect of the corrosive influence is greater, the less the concentration of atoms A in the liquid metal and the higher the saturation concentration of the liquid metal solution. The presence of one atom B in the crack will not in this case cause a change in the bonding force of atoms A - A. After removal of the medium, changes in the mechanical properties of the metal are possible only as a result of irreversible changes in the surface (dissolution) occurring during preliminary holding in the liquid metal.

With the diffusion influence, which is related to diffusion penetration of liquid metal into the solid metal, the bonds broken are not between like atoms A - A, as in the case of adsorption and the corrosion influences, but rather between different atoms A - B (see Figure 153, c).

The condition of the diffusion influence is

$$f_{AB}'' < f_{AA}''^0. \quad (247)$$

The degree of corrosive influence is greater, the stronger an inequality (247) and the higher the solubility of the liquid metal in the solid metal. The effect of the diffusion influence is irreversible, and removal of the medium from a surface of the solid metal will not result in restoration of its mechanical properties to the initial level. It should also be noted that at high temperature the change in strength of plasticity of a solid metal may result from an increase in the self-diffusion factor of the metal- the base of the solid solution.

The interaction of atoms of solid and liquid metals in the end portion of a crack with adsorption, corrosion and diffusion influences can be considered identical formally, by introducing a certain equivalent specific rupture work. Usage of this equivalent leads to equations of identical form (181), (226) and (241), which give the values of the strength of the deformed metal when acted upon by a liquid metal radium, as determined by one of the three factors.

The adsorption, corrosion and diffusion factors differ not only in the mechanisms of their influence on the process of rupture of a solid metal, but also in the mechanisms of their plasticizing influence. Thus, it has been shown [375] that adsorption plasticizing results from the effect of reduction of the surface energy barrier $b^2\gamma'$ preventing the movement of dislocation to the surface of the deformed metal. The facilitation of plastic deformation as a result of the corrosion influence of the liquid metal is possible as a result of solution of the surface atoms of the solid metal located in the path of a dislocation moving toward the surface, in the liquid metal [415]. Diffusion plasticizing is apparently possible only at high temperatures. It is manifested as an increase in creep rate of the solid metal in a liquid metal medium and results from an increase in self-diffusion factors of the base metal resulting from penetration of atoms of the medium intercrystalline lattice. At low temperature, diffusion plasticizing does not appear, since the distortion of the crystalline lattice in this case has more influence on the plastic properties of the solid solution (and also more influence on the strength properties) than does the decrease in the atomic bonding forces.

We must note that the influence of the medium on the process of rupture of this solid metal is greater than its influence on the process of deformation. For example, in Chapter V, A, 1, it is shown that with the adsorption influence of liquid metal, the change in rupture activation energy ($2b^2\Delta\gamma'$) is twice as great as the change in the energy of activation required for a dislocation to move to the surface of the metal ($b^2\Delta\gamma'$). As a result of this, the change in the strength and plasticity characteristics (true tensile strength, rupture activation energy, limiting relative elongation) is greater than the characteristics of the plasticizing influence of the medium (yield point, hardening factor, creep activation energy). In particular, this is explained by the fact, noted in Chapter I, Section 1, that when metals are tested for rupture in an adsorption - active liquid metal medium, the stress-strain diagram most frequently corresponds with the diagram produced by testing in an inert medium, right up to the moment of rupture, which occurs, in the liquid metal with considerably less elongation of the specimen. The placement of the stress-strain diagram of a material in liquid metal in the area of lower stresses than the stress-strain diagram of the material in an inert medium is generally much rarer.

In addition to the difference in the mechanisms of the adsorption, corrosion, and diffusion influence of the liquid metal on solid metal, there is also a difference in the kinetics of the influence of these factors. It was demonstrated in Chapter V, C that in the case of the diffusion influence of the medium the

critical value of deformation rate of the metal at which changes in the mechanical properties of the metal are so observed as defined by equation (242), that is the value of critical rate v_d^* is proportional to the value of the diffusion factor for atoms of the medium in the solid metal: $v_d^* \sim D_T$. Equations of the form of (242) can be produced similarly for the critical rate of deformation with the adsorption (v_a^*) and corrosion (v_k^*) influences of the medium. The only difference will be that for the characteristics of the adsorption influence, we will have to replace D_T in the equation like (242) with the coefficient of surface migration of atoms of the medium into a crack D_M , or in case of the corrosion influence - with the coefficient of diffusion of atoms of the deformed metal into the liquid metal D_ℓ . Assuming in the first approximation that δ is similar in all three inequalities, written for the three forms of liquid metal influence, we produce

$$v_a^* : v_k^* : v_d^* \approx D_M : D_\ell : D_T. \quad (248)$$

Since the rate of surface migration is considerable greater than the rate of diffusion into the liquid metal, while this rate is greater than the rate of diffusion in the solid metal, that is $D_M > D_\ell > D_T$, we find the following relationship of the values of the critical rates of deformation of the solid metal: $v_a^* > v_k^* > v_d^*$. Thus, if a liquid metal medium is capable of influencing a solid metal by adsorption, corrosion and diffusion, in tensile testing of specimens with various deformation rates the diffusion influence will disappear first, followed by the corrosion influence, and the adsorption influence will disappear only at the highest deformation rates.

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